AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **4**, 426 (1936); doi: 10.1063/1.1749874
View online: http://dx.doi.org/10.1063/1.1749874
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/4/7?ver=pdfcov
Published by the AIP Publishing

An Effect of Ultrasonic Radiation on Electrodeposits

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(Received April 21, 1936)

It has been shown by Wood and Loomis[1] that ultrasonic radiations will produce ripples in a coating of warm paraffin on a glass tube placed with its lower end in the oil over a vibrating quartz plate. The authors have observed that similar ripples are produced in cathodic electrodeposits of several metals and alloys when plated under the conditions described below.

Sound waves having a frequency of about 1700 kilocycles were generated by a piezoelectric quartz crystal, 2.54 cm in diameter and 0.154 cm thick placed between brass electrodes and excited by a 250-watt oscillator. A 50-cc beaker containing the electrolyte was placed directly over the top electrode with a film of oil between the electrode and the ground glass bottom of the beaker. The cathode was placed directly over the center of the crystal between two electrodes, as shown in Fig. 1. Neither the cathode nor the anode touched the beaker.

Table I summarizes the results and gives the conditions under which the electrodeposits were formed. The electrodeposited brass mentioned in the table had a composition of about 30 percent Zn and 70 percent Cu, while the composition of the black nickel was about 65 percent Ni, 10 percent S, and 25 percent Zn. The alloys were tried in order to determine whether there would be any great difference in composition on the deposit in the thick part of a ripple as compared to that in the thin part. In the case of brass, if there should have been such a difference there would have been a difference in color of the deposits in the two places. No such difference was observed.

The velocity of the sound waves in the liquid, computed from measurements of the distance between ripples, taken as a half wave-length, corresponded approximately to that obtained by other methods

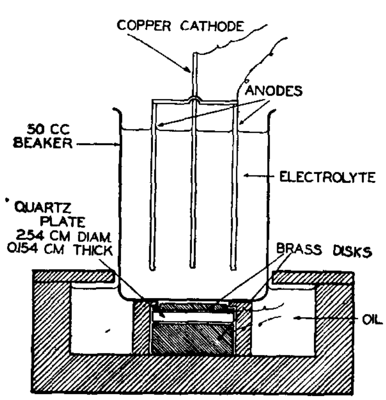

FIG. 1. Arrangement of the electrodes, beaker, and quartz, piezoelectric crystal.

TABLE I

METAL	COMPOSITION OF THE BATH (grams per liter)		CURRENT DENSITY (amp./dm²)	TIME (minutes)	RESULTS
Iron	Ferrous chloride Calcium chloride	300 150	5	60	Very good ripples See Fig. 2
Iron	Ferrous sulphate Magnesium sulphate	200 100	5	60	Good ripples
Iron	Ferrous sulphate Ammonium chloride Sodium citrate	130 100 3	5	60	Fair ripples
Cobalt	Cobalt ammonium sulphate	200	5 5	60 15	Poor ripples Fair ripples
Cadmium	Sodium cyanide Cadmium oxide Sodium hydroxide	75 25 15	5	60	Poor ripples
Chromium	Chromic acid Sulphuric acid	250 3	4	60	No ripples. That deposited in the bath agitated by U.S. was not as bright as a control
Zinc	Zinc sulphate Ammonium chloride Sodium acetate	250 15 15	4	30	Good ripples
Zinc	Zinc cyanide Sodium cyanide Sodium hydroxide	30 30 25	4	30	Fair ripples. That deposited in the bath agitated by U.S. was not as bright as a control
Brass	Copper cyanide Sodium cyanide Zinc cyanide Sodium carbonate	30 45 7.5 15	4 1.5 0.5	30 30 30	No ripples No ripples Fair ripples
Black Nickel	Nickel ammonium sulphate Ammonium sulphocyanate Zinc sulphate	50 50 60	4	30	Good ripples

The temperature of all the plating baths was 47°C.

[1] R. W. Wood and Alfred L. Loomis, Phil. Mag. 4, 417 (1927).

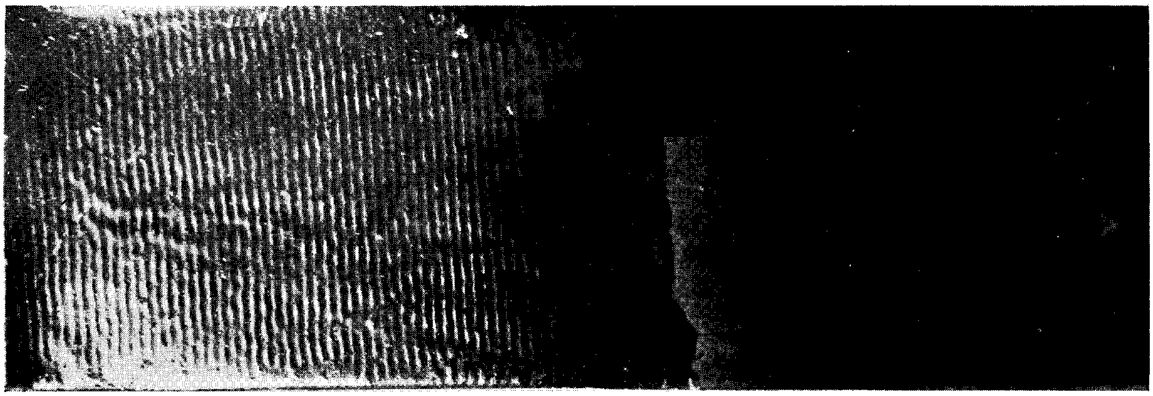

FIG. 2. Ripples in electrodeposited iron produced by ultrasonic radiation (enlarged).

The results seem to indicate that stationary waves are set up in the solution and that the metal ions are relatively more concentrated in layers which are separated by half wave-lengths. In the case of iron and zinc it appears from the results given in Table I that deposits showing the best ripples are obtained from the more concentrated solutions.

JULY, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

The Dispersion of Sound in Oxygen

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(Received April 14, 1936)

The velocity of 1000-cycle sound wave in oxygen of various degrees of humidity at 26.5°C has been measured. The velocity behavior indicates that the water molecules are effective in bringing the heat capacity of the first vibrational state of the oxygen molecule into equilibrium with the sound wave. The dispersion change in velocity amounts to 0.16 percent. Intensity measurements agree with velocity data in fixing the center of the dispersion region between 1 and 3 mm partial pressure of water, which is in agreement with the values calculated from Knudsen's studies of rates of decay at higher frequencies.

THE classical work of Knudsen and Kneser[1, 2, 3] on the rates of decay of sound waves in mixtures of air and water vapor, and oxygen and water vapor, showed that there was an optimum humidity at which the rate of decay has a maximum value, and showed definitely that the effects observed were due to the efficiency of water molecules in activating the first vibrational state of the oxygen molecule and in returning this vibrational heat capacity to the sound wave. On the basis of the recently developed theory of sound dispersion[4, 5, 6] there should be an anomalous behavior in velocity accompanying the appearance of a maximum rate of decay. The velocity of sound in air and oxygen has been determined by several investigators.[7, 8, 9] Pierce originally reported that at audiofrequencies measurements in dry air and in air at 36 percent and 55 percent humidity indicated no change in velocity with change in humidity within an accuracy of 0.021 percent.

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