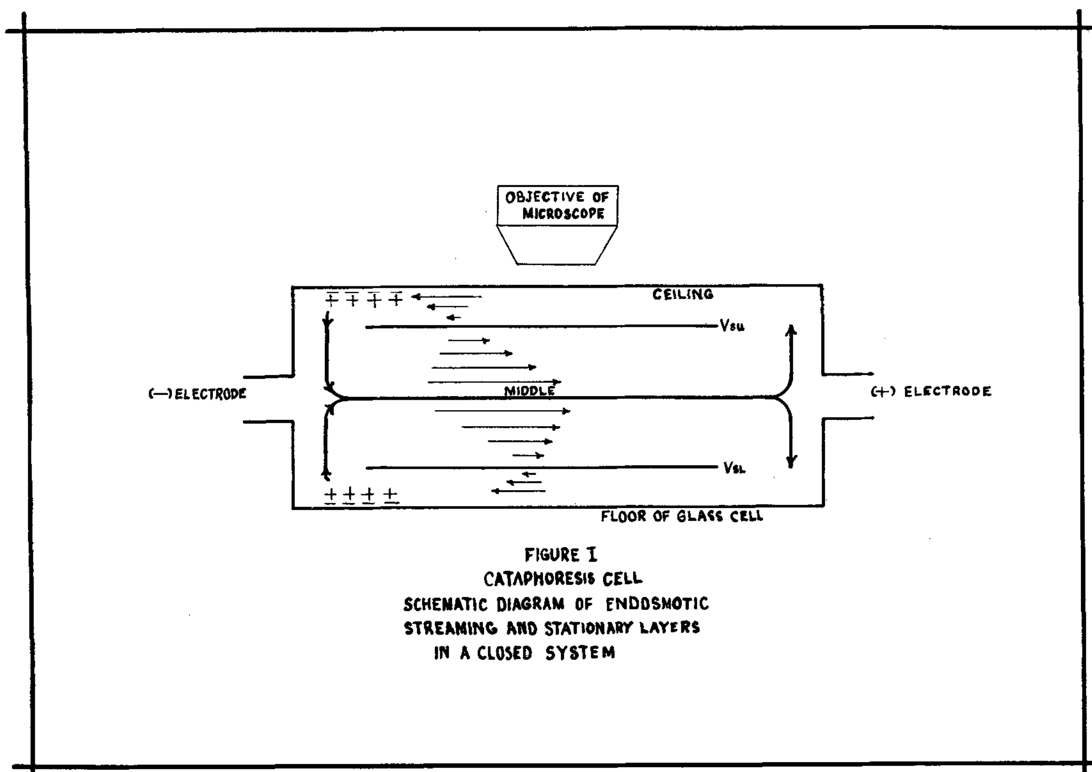

FIGURE I
CATAPHORESIS CELL
SCHEMATIC DIAGRAM OF ENDOSMOTIC STREAMING AND STATIONARY LAYERS IN A CLOSED SYSTEM

Electrical Measurements Of Oil Droplets

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IT is assumed that when an oil globule is suspended in ordinary aqueous menstrua there exists about the globule an electrical double layer. When the globule is negatively charged, there is a layer of negative electricity on the surface of the oil, while in the liquid of the menstruum immediately surrounding it there is a corresponding layer of positive electricity.

When we place the oil-in-water emulsion in an external electrical field the oil globules migrate toward the positive electrode, hence it is inferred that the globules carry negative charges. The origin of the electrical charge is not known and thus far we have no clue other than some empirical theories to account for the phenomenon.

A convenient type of apparatus for these measurements has been described by Northrop[1]. The data presented in this work are electrical measurements made with a modified Northrop-Mudd Assembly*.

When cataphoresis is conducted in a closed system, the electrical double layers between the fluid and the walls (glass) are located in the positions shown in the schematic diagram (Fig. 1).

Under the influence of the applied electrical field the electrical layers in the water are given a positive velocity to the cathode and drag the successively contiguous layers of water along at lesser and lesser velocities. The return streaming of water occurs in the middle of the cell. Hence the suspended fat globules vary in their cataphoretic mobilities at different levels

[1]Northrop, J. H., Journ. Gen. Physiol., 4, 629, 1921-2.
Ibid., 635, 1921-2.
Ibid., 7, 729, 1925.
*Arthur H. Thomas Company.

in the cell and the true velocity is observed only in the stationary layers. The microscope is for this reason focused on either the upper or lower stationary layer for the determination of the true mobilities.

The cell is calibrated as follows: fill the cell with water. Bring the calibrated head of the fine adjustment screw to zero and focus the microscope* on the inner floor of the cell. Then turn fine adjustment screw until the microscope is focused on the inner ceiling of the cell, determining the depth of the cell chamber in units on the head of the fine adjustment screw.

Using the formula given in this paragraph, focus the microscope on the upper or lower stationary level. Never change this focus unless you need to recalibrate the cell. The stationary layers are fixed at a distance of $\frac{1}{2}$ D ÷ $\sqrt{3}$ above and below the middle of the cell. For example, if a cell is 100 units deep on the micrometer screw head, the middle is 50 units; $\frac{1}{2}$ Depth = 50; and 50 ÷ $\sqrt{3}$ = 28.9; hence the lower stationary level (V_{sl}) is located at 21.1 units from the floor of the cell and the upper (V_{su}) at 78.9 units from the floor. All cataphoresis measurements are made at one or the other of these layers.

As a source of current we use "B" batteries (3 sections) giving an impressed voltage of 140 volts. The apparatus consists of a pair of non-polarizing zinc-zinc sulphate electrodes with two-way stopcocks and a system for filling the chamber (Fig. 2). The current is controlled from a switchboard consisting of a reversing switch so that the polarity of the electrodes can be reversed quickly. A voltmeter is needed in the circuit to show that the impressed potential is constant and an ammeter to show that practically no current (or less than 10 milliamperes in H_2O) is flowing, and hence indicating that the emulsion is a poor conductor. To actually make the measurements throw on the voltage and determine the time in seconds and fractions of a second (good stop watch, 1/10 sec.) that it takes an oil globule to pass the diameter of two or more squares on the ocular micrometer. Make ten measurements and then reverse the orientation of the electrical field by reversing the switch and repeat the measurements in the opposite direction. Average the measurements. Calculate the velocity in micra per second[2]. The absolute charge in millivolts need not be calculated.

In addition to the ocular micrometer which usually is ruled in squares too large to measure the diameters of the oil globule, a binocular attachment to the microscope may be used. In the other eyepiece may be placed a micrometer ruled in the usual 1 μ spaced line. Otherwise the finely ruled micrometer can be placed in the original ocular of the microscope. Thus measurements can be made simultaneously of the mobility and diameter of the globule.

Mooney[3] found that the electrical mobility of oil droplets increased with increasing radius. Perhaps this variation in mobility with size may be related to changes in surface rather than to a purely frictional phenomenon. The addition of a trace of electrolyte serves to stabilize the mobility so that large and small oil droplets migrate with approximately the same velocity. Mooney found that in pure water, for an electrical field of 10 volts/cm the mobility increased with the diameters of the globules for the range 0.005 to 0.04 mm. Mooney says that the results obtained seem to indicate that as the diameter increases, the mobility approaches asymptotically an upper limit. Whether the lower limit, as D approaches zero is zero or finite is hard to judge from the curves so far obtained. He showed with emulsions of Stanolind in 0.0008 N $CuSO_4$ that the cataphoretic mobility of the globules is independent of their diameter. From 1 μ to 18 μ the mobility in case of a pure oil in 0.0008 N $CuSO_4$ is independent of size.

We tested several pure lubricating oils (steam and combustion engine oils) by the method of cataphoresis and found multiple mobilities in conductivity water emulsions, whereas in dilute copper solution the globules measured showed identical velocities regardless of size (1-16 μ). Differences were shown to exist in the different types of lubricating and other mineral oils. In oils purposely mixed, "split" mobilities were observed in the electrolyte emul-

*Objective, 8 mm., 0.50 N. A., 21X, (long focal working distance.)
Ocular, —25X, compensating.
Ocular micrometer 25 micra square rulings or a Sedgwick-Rafter ruling placed in diaphragm of ocular.
Calibrate with stage micrometer.

[2]L. B. Jensen et al. Electrophoresis of Diphtheria Bacilli, I, II, III, Journ. Bact. XV, pp. 367-450, 1928.
[3]M. Mooney, Phys. Rev., 23, p. 396, 1924.

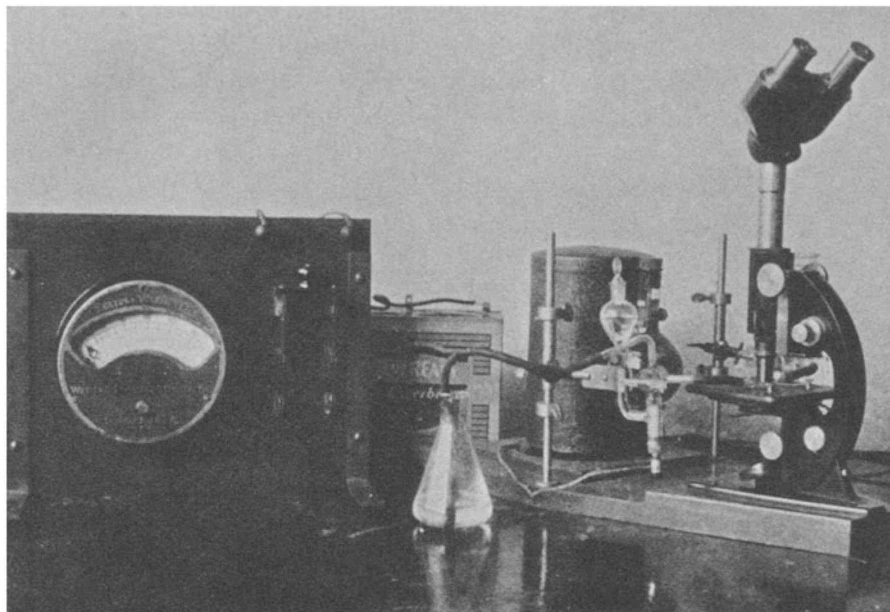

Fig. 2

sions. It is theoretically possible that this method may help elucidate the engineers' question of emulsification of a given oil in forced feed lubrication of steam turbines, etc.

It occurred to us that the method of cataphoresis might serve to identify an oil or fat, and perhaps adulterated or mixed oils also could be detected by these physical measurements. Accordingly 55 samples of various oils, the histories of which we knew, were tested as emulsions in conductivity water and emulsions in dilute copper solution.

About 1cc of oil was added to 100 cc of menstruum and emulsified by shaking vigorously in a shaking machine. The emulsion was then removed from the excess oil and after standing five minutes each emulsion was measured in the cataphoresis apparatus. The temperature of the menstrua was 25° C in each case.

The data of measurements in conductivity water are not included in this report since they are of academic interest only. The mobilities of the oils in 0.0008 N $CuSO_4$ are recorded in Table I. Each test was run in duplicate. The data are recorded in order of increasing magnitudes of charge on the droplets.

It will be observed that these data show no correlations with any of the known physical, chemical or physiological characteristics of fats and oils. It appears that the refined oils may possess mobilities that might serve to identify them. However, there seem to be no sharp lines of differentiation which can assure the observer that he is dealing with a specific oil.

The "split" mobilities of rancid oils are of some interest. The crude oils also appear to present manifold velocities in the same emulsion. Hydrogenation appeared to lower the potential of an oil. The presence of nickel in one batch of herring oil lowered the electrical charges markedly.

When two or more "pure" refined oils are purposely mixed in equal volumes multiple mobilities are observed. For example:

Oil No. 3. . peanut oil "A" = 15.6 micra per sec.
Oil No. 13. cotton oil = 22.7 micra per sec.
Oil No. 54. coconut =55.5 micra per sec.

when mixed in equal quanities and then emulsified in the copper solution showed the following groups of velocities:

16. 0 to 20.0 — Twenty droplets
(micra per 21.0 to 48.0 — Twenty droplets
sec.) 52.0 to 55.5 — Twenty droplets

It is obvious that the electrical method, so far as it is now developed, furnishes us at best only presumptive evidence as to the identity of an oil or mixed oils. Perhaps varying amounts of the natural components of an oil, stearine, etc., preclude any exact analysis by this means. The values of the method can be determined only as the results of wider experience become available.

TABLE I
OIL EMULSIONS
P. D. (ELECTRICAL CHARGE) IN 0.0008 N $CuSO_4$

		P. D. μ/sec. 140 V. D. C.
1.	Butterfat (summer cream)	11.1
2.	Herring oil "B" Hydrog. 32.7° titre, nickel not all removed	12.5 to 25.0
3.	Peanut (No. A) refined 12° B	15.6
4.	Peanut (No. A) refined 14° B	16.6
5.	Hardened "fish oil"	16.6 to 28.0
6.	Hardened whale oil	16.1 to 25.0
7.	Peanut oil crude, unknown history	16.6 to 25.0
8.	Peanut oil refined, sample No.7	15.6 to 26.3
9.	Castor oil rancid	16.6 to 47.6
10.	Hydrogenated cotton	20. to 26.3
11.	Oleo stock	20. to 33.3
12.	Peanut crude "A"	22.5 to 33.3
13.	Cotton oil pressed, refined	22.7
14.	" " " "	22.7
15.	" " " "	22.7
16.	" " " "	22.7
17.	" " " "	23.3
18.	" " " "	23.3
19.	" " " "	25.0
20.	" " " "	25.0
21.	" " " "	25.0
22.	" " " "	25.0
23.	" " " "	25.0
24.	Cotton oil "A"—14° Beau lye	25.0
25.	Cotton oil "A"—12° Beau lye	25.0
26.	Cotton oil rancid	25.0 to 29.0
27.	Cotton oil rancid	25.0 to 29.2
28.	Sunflower oil, unknown purity	26.6
29.	Sunflower oil, pure	26.6
30.	Neat's foot	28.0
31.	Crude Cottonseed "A"	27.7 to 29.0
32.	Herring oil "B" hydrog. 32.7°, all nickel removed	30.0
33.	Corn oil "A" refined 18° Beau lye	31.0
34.	Corn oil "A" refined 16° Beau lye	31.2
35.	Soya-bean "A" refined 14° Beau lye	31.0
36.	Mustardseed oil	33.0 to 25.0
37.	Palm kernel oil	33.0 to 28.5
38.	Sesame oil, unknown purity	28.5 to 50
39.	Olive Oil rancid	30.3 to 42.0
40.	Crude palm oil	31.2 to 40
41.	Soya-bean refined	33.3
42.	Crude Soya-bean "A"	33. to 50
43.	Crude peanut	33.3 to 41.6
44.	Lard kettle rendered	35.6
45.	Coconut, crude	35.7
46.	Herring oil bleached but not caustic refined	38.0
47.	Kapok oil	38.6
48.	Soya-bean "A" refined 12° Beau	38.4
49.	Corn oil	40.0
50.	Perilla oil	43.1
51.	Pilchard bleached and filtered	45.4
52.	Palm—refined and deodorized	50.0
53.	Pilchard crude	55.0
54.	Coconut refined	55.5
55.	Corn oil crude	62.0