

On the Electric Resistance of Solid Soap

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PREVIOUSLY we reported (1) that commercial soaps show very complex physical changes above about 40°C. The effects of impurities and conditions of treatment on the electric resistance of solid soap have been studied (2). In the present paper we describe measurements of electrical resistance in solid soaps at various temperatures and with various water contents.

Four crystalline forms of soaps are known (3), the most important of which is the ω -form of unmilled soap and the β -form found mostly in milled soap. The formation and disappearance of these crystalline forms are known to be influenced to a large extent by manufacturing conditions (3, 4). Therefore heat-treated samples, which are presumed to be ω -form, were first investigated. Later, samples made with and without heat treatment were compared.

Experimental

Figure 1 is a schematic diagram of the apparatus used. A glass sample tube 18 mm. in diameter was equipped with platinum electrodes (3 × 12 mm., 10 mm. apart) connected with an automatic resistance recorder (made by Yokogawa, E. W.). A tiny thermometer was placed at the center of the tube. The apparatus was immersed in an ice bath or an oil bath, as desired.

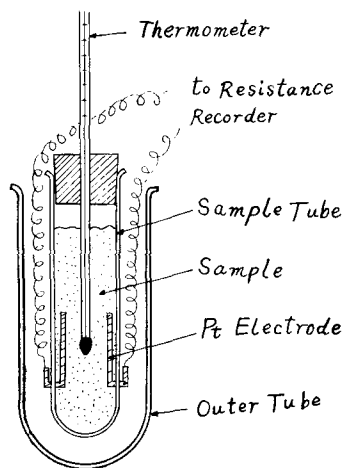


FIG. 1. Apparatus.

Neat soap, containing 30% water, was air-cooled and solidified at room temperature. Soap containing less than 30% water was obtained by air-drying soap chips. For soaps containing more than 30% water, the necessary amount of water was mixed with air-dried soap by heating since water cannot be readily mixed with neat soap. The soap was made from a mixture of beef tallow, coconut oil, and some hardened oil. The constants were:

Melting point.....	40°C.
Neutralization value.....	39.1
Iodine value.....	0.01%
NaOH.....	0.83%

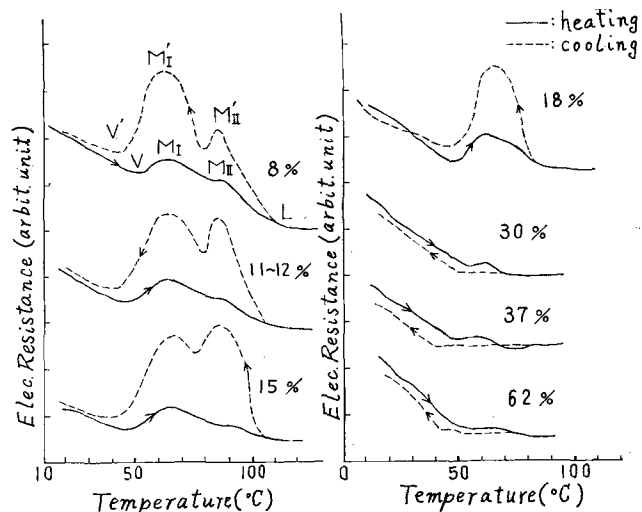


FIG. 2. Effects of temperature changes on the electrical resistance of soaps containing various amounts of water. (Electrical resistance is shown in arbitrary units.)

NaCl.....	213.4
Glycerine.....	about 2%

Soap in the sample tube was melted, deaerated as completely as possible, cooled until solid (and left overnight). During measurement of the electrical resistance the temperature was changed at a rate of 0.5–1.0°C. a minute.

Water content was precisely determined for each sample removed from between the electrodes.

Results

Effect of Heating (Figure 2)

a) Less than 18% water in soap—At first, the electrical resistance decreases slightly as the temperature increases, reaching a minimum at 40–50°C. (point V). As the temperature is raised farther, resistance increases to a maximum at 60–65° (point M_I), then decreases to a second shallow minimum at about 80°, and increases to a slight maximum at 86–90° (point M_{II}). Finally the rate of decrease becomes extremely slow as the soap melts.

b) Between 18 and 30% water—The resistance-temperature curve is similar to a) except that the second minimum and maximum are absent because the melting point of the soap is below 80–85°.

c) Above 30% water—There is a fairly steady decrease in electrical resistance as temperature is raised, with a slight increase as the soap begins to melt.

Effect of Cooling from Molten State (Figure 2)

a) Below 30% water—The temperatures of maxima and minima in the resistance curves during cooling are at the same points as during heating. However the changes in resistance are many times more pronounced during cooling than during heating.

b) Above 30% water—The cooling curves are practically identical with heating curves but are slightly lower.

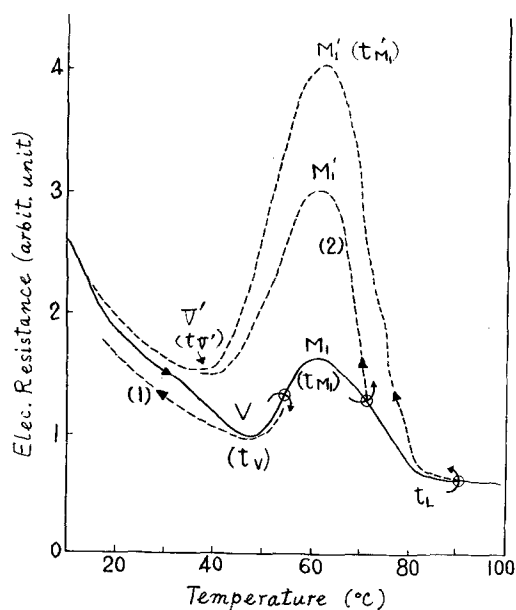


FIG. 3. Hysteresis in electrical resistance vs. temperature curves for soap of 20% moisture content.

Hysteresis Effect (Figure 3)

In the case of the soap containing 20% water (Figure 3), samples were heated and then cooled from various temperatures below the melting point.

a) As is shown in curve (1), when the temperature was decreased at the usual rate (0.5–1.0°/min.) from a temperature below t_{M_1} , electrical resistance values during cooling and heating were practically identical.

b) Curve (2) shows that when the soap was heated to a temperature slightly above a t_{M_1} and then cooled, there was a sharp increase in electrical resistance. A similar effect was observed at all temperatures between M_1 and L (the melting point). It seems that t_{M_1} is the critical point above which hysteresis effects appear.

Effect of Stepwise Temperature Changes (Figure 4)

In the preceding experiments the rate of both heat-

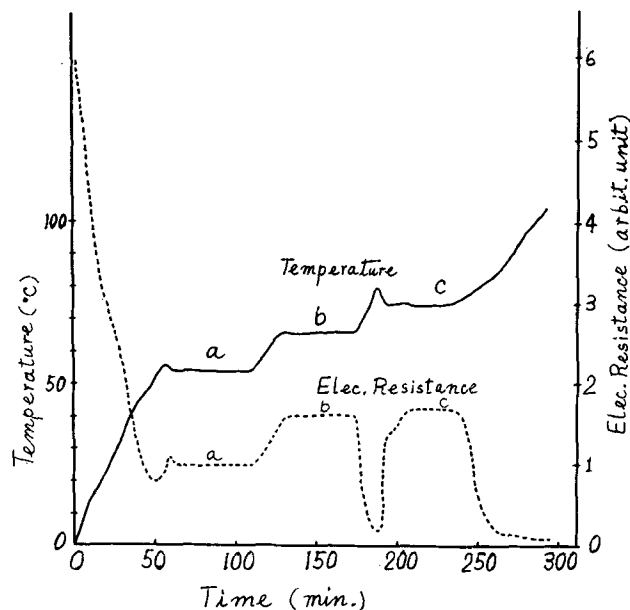


FIG. 4-1. Electrical resistances of soap (17.3% moisture content) during stepwise heating.

ing and cooling was 0.5–1.0°C./min. For another extreme case the temperature was brought to a given point and kept constant for at least 30 min. Figures 4-1 and 4-2 show measurements for heating and cooling, respectively, of a soap containing 17.3% water. From these curves it was concluded that, for all points except C, resistance values were constant at a given constant temperature. The relatively large values at C may be attributed to hysteresis since the sample

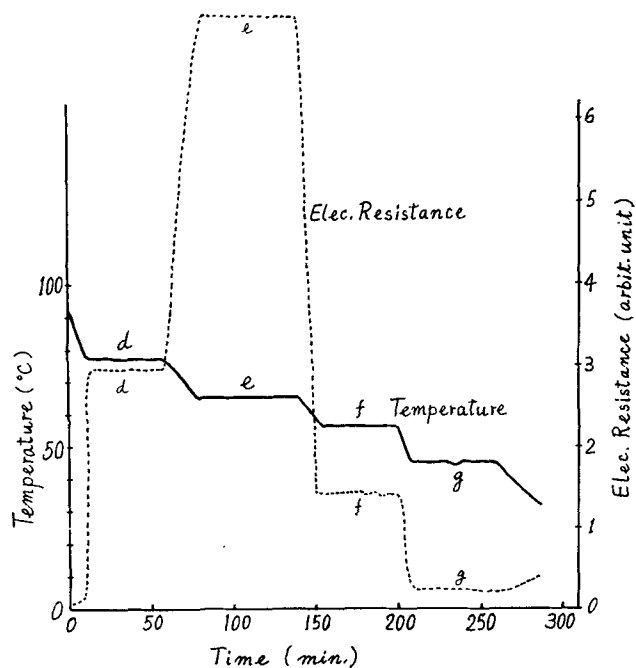


FIG. 4-2. Electrical resistances of soap (17.3% moisture content) during stepwise cooling.

was accidentally overheated slightly and then cooled to the proper temperature.

Whenever soap is held at a given temperature, its electrical resistance is constant and the hysteresis effect appears independent of the rate of heating or cooling.

Discussion

When logarithms of conductivity vs. $1/T$ curves for various water content, where T is absolute temperature, are drawn from the relation in Figure 2, it may be more clearly shown that those curves consist of three parts. Both in the regions below 40°C. (V') and above L , all curves are practically parallel to each other, showing that they are in the same state of phase, independently of water content. It is also interesting to note that there appear maxima or minima always at around the same temperature in the third intermediate region between 40°C. and L . It would appear that these changes are caused by phase transition.

Figure 5 shows the curves connecting the points where definite maxima and minima in electrical resistance were observed.

McBain (6) presented a phase diagram for soap based on studies of vapor pressure, dilatometry, and optical measurements. The melting line t_L (Figure 3) corresponds well with McBain's T_c curve. Similarly the line connecting the points M_1 for various water contents in Figure 3 fits the horizontal line at 60°C. in McBain's diagram, and region between t_{M_1} and t_L was also found to be heterogeneous. Our data however

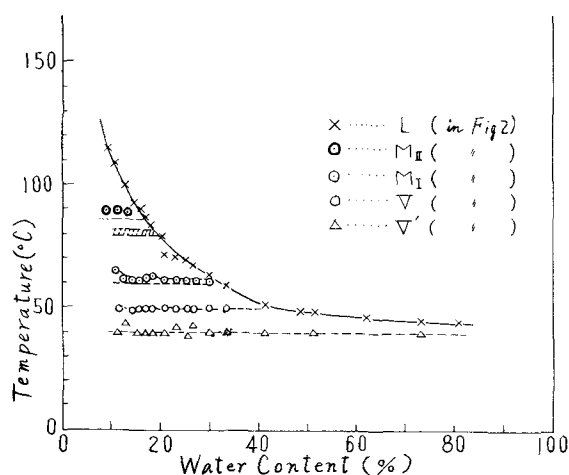


FIG. 5. Phase transition points for soaps of various moisture contents shown by electrical resistance values. (L, M_{II} , etc., refer to corresponding points in Figure 2.)

seem to indicate phase transitions at about 50° and 40°C., which were not found by McBain.

Thiessen and Stauff (5) have noted that there are phase changes near the melting point of the constituent fatty acids in a soap and have named this the "genotypic point." Since fatty acids in commercial soap have a melting point around 40°C., the horizontal line at this temperature in Figure 5 may be the "genotypic point."

Studies with single pure soaps (7) have shown that transition points are practically independent of water

content. For the sodium soaps of lauric to stearic acids, conductivity decreased to a minimum between 80° and 90°C., after which it started to increase again. This effect was independent of the kind of fatty acid or water content. It appears that these effects may predominate at around M_{II} of Figure 2.

Summary

Electrical resistance values are reported for soaps of various moisture contents. Marked changes in resistance were found at 40–50°C. Below this temperature the logarithm of conductivity is a linear function of inverse temperature, and the slope of the curve is practically independent of water content. Above 40° resistance is markedly affected by the water content of the soap. For soaps containing 12–30% water, heating and cooling curves show definite maxima and minima in electrical resistance values. This effect is less obvious in soaps containing more than 30% water. The phase transition points estimated from resistance measurements are in good agreement with those deduced from other physical measurements.

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Flash Desolventizer Operation to Produce Soybean Protein Flakes¹

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SOYBEAN PROTEIN FLAKES are useful for many industrial applications, for example, in preparing plywood or paper-coating adhesives. However flaked, hexane-extracted soybeans are not suitable unless precautions are taken to minimize denaturation because of heat treatment incurred in the desolventizing operation. Previous results obtained by Belter *et al.* with a flash desolventizer indicated that such a unit is well suited to hexane removal without extensive protein denaturation (2). However the effects of process variables were not studied; moreover aged soybeans with partially denatured protein were used. The present investigation was undertaken to establish desirable process conditions for flash desolventizing hexane-extracted flakes without significant protein denaturation. Soybeans from a current harvest were used.

The flash desolventizer process employs superheated vapors in direct contact with solvent-wet feed to pro-

vide the heat required for vaporization of solvent and to convey solids through the desolventizing tube to a cyclone separator. A major portion of these vapors is reheated and recycled, and the remainder is sent to a condenser. This desolventizing process combines certain features of a horizontal, vapor type of desolventizer (4) with those of a flash or pneumatic conveying drier.

The performance of a flash desolventizer is determined by several factors that control the heat transfer rate and consequently the rate at which entrained solvent is vaporized. One of the most important is the direct contact obtained between solids and superheated vapors whereby the flakes' extensive surface area is fully used for heat transfer. Turbulent vapor flow in the desolventizing tube and a high temperature differential at the solids inlet also increase the rate. As the solids are simultaneously dried and carried to the cyclone separator, the temperature differential progressively decreases. Meanwhile solvent and moisture evaporating from the solids moderate the latter's temperature rise. The high heat-transfer rate, combined with the thin flakes, permits rapid solvent

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