ON THE DISINTEGRATION OF THE STARCH PASTE CAUSED BY THE IRRADIATION OF ULTRASONIC WAVES.

By Sôzaburo Ono.

I. Introduction

It has been observed by Szalay[1,2] and other investigators[3-8] that the highly polymerised compounds are changed into lower polymerised compounds by the disintegrating action of ultrasonic waves. Szalay also found out that soluble starch becomes dextrine,[1] and he considered the mechanism of this disintegration as follows. In the field of ultrasonic waves, large soluble starch particles are forced to vibrate under the influence of violent, oriented vibration of the water molecules acting as the medium. Consequently, in spite of very slight temperature elevation of the water molecules, the temperature of starch particles rises remarkably because of their larger size. Thus Szalay considered the mechanism of disintegration as a hydrolysis by local heating. Many other mechanisms should, however, be taken into account for the disintegration of highly polymerised compounds, especially of such a large granule as that of native starch now in question. Of these mechanisms only the main three will be mentioned here. The first is the "cavitation".[9,10] Among older biological researches made by utilizing ultrasonic waves, there are some studies on destruction of animal and vegetable organisms.[11,12,13] Schmidt and Uhlemeyer[12] attributed the destruc-

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1) A. Szalay, *Z. phys. Chem.* [A], **164**, 234 (1933).

2) A. Szalay, *Phys. Z.*, **35**, 293 (1934).

3) S. Brohult, *Nature*, **140**, 805 (1937).

4) M. Kasahara and K. Kawanishi, *Klin. Wschr.*, **16**, 1191 (1937).

5) E. Thieme, *Phys. Z.*, **39**, 384 (1938).

6) N. Sata, *Kolloid Z.*, **87**, 186; **88**, 182 (1939).

7) H. Freundlich and D. W. Gillings, *Trans. Farad. Soc.*, **34**, 649 (1938): **35**, 319 (1939).

8) G. Schmid and O. Rommel, *Z. Elektrochem.*, **45**, 659 (1939): *Z. phys. Chem.* [A], **185**, 97 (1939).

9) Cavitation is a phenomenon that as soon as the hydrostatic pressure in a liquid is reduced to the vapour pressure of the liquid, two phases (vapour and liquid) may be formed (formation of cavity) and then the cavity thus formed is collapsed. (collapse of cavity)

10) Lord Rayleigh calculated the pressure developed during the collapse of a spherical cavity. Calculation shows that pressures of 1250 atmospheres may develop at the moment when the cavity collapses to the 1/20 of its original diameter. Intense ultrasonic vibrations may be a cause of this cavitation process. Accordingly a strong mechanical effect may be performed by the cavitation thus produced.

11) L. Bergmann, "*Ultraschall*" V. D. I. (1939); E. Hiedemann, "*Ultraschall*" Walter de Gruyter (1939); A. Dognon u. E. u. H. Biancani, "*Ultra-sons et Biologie*" Gauthier-Villars (1937); N. Marinesco, "*Propriétés piézo-chimiques, physiques et biophysiques des ultrasons*" Bd. II. Hermann and Cie (1937).

12) F. O. Schmidt and B. Uhlemeyer, *Proc. Soc. Exp. Biol. Med.*, **27**, 626 (1930).

13) C. H. Johnson, *J. Physiology*, **67**, 356 (1929).

tion of protoplasm to the formation of gas bubbles, because the destruction was reduced when the formation of gas bubbles ceased due to increased external air pressure. Johnson[13] found that the destruction does not occur when a system containing protoplasm or red blood cells is placed under increased external pressure or when the air is replaced with more soluble gases to prevent the formation of gas bubbles or when it is evacuated. He thus attributed the phenomenon to the expulsion of gas bubbles out of cells. Whatever the explanations may be, the experimental results can be also explained in such a manner that disintegration by ultrasonic waves depends chiefly upon the cavitation in the sense above described.[9] Afterwards, Freundlich and Söllner[14] investigated qualitatively the influence of external air pressures on such a phenomenon as the liquefaction of thixotropic gel, and obtaining similar results to those of Schmidt and Uhlemeyer[12] and Johnson[13] they regarded the liquefaction as caused by the cavitation. Freundlich and Gillings[7] also attributed the reduction of viscosities of various colloidal solutions to the cavitation.

The second mechanism is that of Smith's theory[15], namely, the destructive mechanical effect by the pulsation of gas bubbles. The third mechanism is the one proposed by G. Schmid while the present report was under preparation. According to him a pure mechanical force, such as the vibration of particles of the medium, is proved to be capable of grinding down such a substance as polystyrol. With regard to the disintegration of starch, further studies on its mechanism are required. The object of the present report is to make clear the nature of disintegration of granules of native starch paste and to elucidate the mechanism of the disintegration.

II. Exprimental

a) **Materials**:—Potato starch (starch of the Japanese pharmacopoeia) and wheat starch obtainable at market were used without any purification. The quality of the starch paste varies according to the methods by which it is made. In the first half of the experiment, a mixture of starch and water was shaken

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14) H. Freundlich and K. Söllner, *Trans. Farad. Soc.*, 32, 966 (1936).

15) F. D. Smith, *Phil. Mag.*, 19, 1147 (1935): The gas bubbles generated when the cavitation is occurring or those existing originally in the liquid are considered, when they are extremely small, to be oscillated radially by sound waves. Only the bubbles having a certain radius are possible to resonate with the frequency of ultrasonic waves. Such resonant bubbles cause a very large strain in the liquid and the vibration of bubbles smaller than the resonant bubbles, also, causes more than a thousand times as large strain as that in the case without bubbles. Thus Smith explains the destructive action of ultrasonic waves.

with hands and its temperature was raised above room temperature: after reaching 50°C., the temperature was elevated to 80°C. in 30 minutes, nearly at the rate of 1°C. per minute, and then promptly up to 95°C., at which the mixture was left to stand for 60 minutes, and thus the paste was made. In the latter half, heating procedure was the same, but, instead of shaking with hands, a glass stirrer used to agitate. The number of rotation was about 200 R/M below 75°C. and about 100 R/M above 75°C. By these two methods pastes of much the same quality were obtained.

b) Experimental methods:—Primarily the viscosity of paste was measured, and secondarily the observation of microscopic structure of paste particles was made.

Regarding solvated solutions of highly polymerised compounds, there are many viscosity formulae, one of which is that of Kunitz[16]:

$$\eta=\frac{1+0.5\Phi}{(1-\Phi)^4} \qquad (1)$$

where η is the relative viscosity of the disperse system to the solvent, and Φ is the fraction of the volume to be occupied by disperse particles in the disperse system. Tables I & II show the values of Φ obtained from formula (1) by measuring the viscosities of the potato and wheat pastes made by the methods above described. In both tables, the concentration, C, and Φ are represented by % and the fourth column, $\Phi/C\equiv\varphi$, indicates the specific volume, that is, the volume to be occupied by 1 g. of the starch particles in the paste. In the case of the potato paste, this viscosity formula is applicable in the concentration range 0.01 ~ 1%, and apparently 1 g. of the starch particles occupies a volume of 67.7 c.c. In the case of wheat starch, though made by the same method, $\varphi=13,4$ in

Table I.

φ of the Potato Paste

C (%) Concentration	η Relative Viscosity	Φ (%) Volume Fraction	$\Phi/c\equiv\varphi$ Specific Volume
1	77.9	63.9	63.9
0.5	7.14	35.1	70.2
0.1	1.39	7.15	71.5
0.05	1.13	3.25	65.0
0.01	1.03	0.68	68.0
			Mean=67.7 (c.c.)

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[16] M. Kunitz, *J. Gen. Phil.*, 9, 715 (1926).

Table II.

φ of the Wheat Paste

C (%) Concentration	η Relative Viscosity	Φ (%) Volume Fraction	$\Phi/c \equiv \varphi$ Specific Volume
2	6.0	33.5	16.7
1	1.97	14.3	14.3
0.5	1.34	6.4	12.8
0.1	1.07	1.57	15.7
0.05	1.025	0.55	11.0
0.01	1.005	0.10	10.0
			Mean=13.4 (c.c.)

the range 0.01~2%. By measuring the variation in the quality of paste caused by ultrasonic waves as the variation in the value of φ and that in microscopic structure, the mechanisms of disintegration of the paste will be discussed.

c) **Apparatus for generating ultrasonic waves**:—Fig. 1 shows the electric circuit: the maximum output of the oscillator valve was 200 watts and the frequencies used were 470 KH_z and 800 KH_z, the latter chiefly being used.

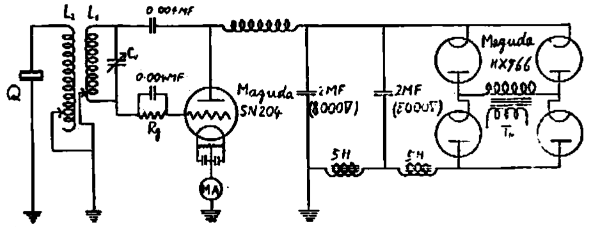

Fig. 1—Electric circuit for generating ultrasonic waves: Q, Quartz (dia.=40 mm, 800 KH_z); C, 1000 MMF (5000V); L_1, dia.=22 cm, 21 turns; L_2, dia.=11 cm, 89 turns; Rg, 10,000Ω; T, step up to 1,500V.

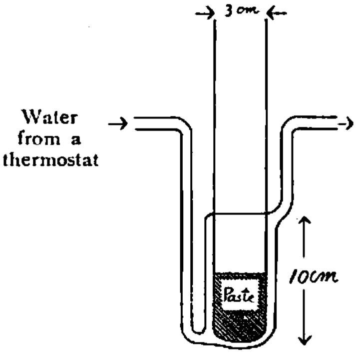

Fig. 2—Reaction vessel A.

d) **Experimental procedure and accuracy of measurement**:—For the irradiation of ultrasonic waves, the sample was held in a double walled glass vessel (reaction vessel A), around which water from a thermostat circulated as shown in Fig. 2. Thus the temperature of the paste was kept constant within about 1°C. After the influence of the temperature of the paste upon the disintegration effect was found to be negligible, two kinds of single walled test tubes were often used, which were almost the same in diameter as reaction vessel A. One of them was thin walled (reaction vessel B). The other was thick walled (reaction vessel C), and was used in the experiments carried out under higher or lower external air pressures.

In order to measure viscosity, Ostwald viscosimeters were used, at a temperature of 40°C. ±0.05°C. The viscosimeters were divided into three groups according to the inside diameter of the capillary part, and a viscosimeter of thicker type was used for the paste of higher viscosity. For example, in the case of 1% potato paste, a thick viscosimeter 2 mm. in inside diameter was used from the paste not yet treated by ultrasonic waves to the paste of $\varphi=50$. The viscosity, in this case, was obtained by measuring the relative viscosity to glycerine preliminarily measured and converting the value thus obtained into the relative viscosity to water. When viscosity was high, the observed values were incorrect, that is, the values varied in every measurement for the same paste before the irradiation of ultrasonic waves. To remove this error, however, the mean of the five observed values was adopted. Since different viscosimeters pointed different readings even for the same paste, the mean reading of two viscosimeters was taken. But the error of 4.6% of η and 0.5% of φ could not be removed. As the disintegration went on, the accuracy of measurement increased and in the case of 1% paste the observed values were in so fairly agreement below $\eta=2.5$; $\varphi=18.6$ as to be reproducible.

III. Exprimental Results

(A) Disintegration curve (φ-time curve)—Influences of frequencies—Comparison with heat treatment.

The decrease in φ with the time in the case when the paste has been irradiated by ultrasonic waves is shown in the real lines in Fig. 3. The experiment was carried out under the conditions: a reaction vessel A, temperature of the paste$\equiv T=30$°C., the distance from the quartz plate to the reaction vessel$\equiv D=$ 50 m.m., volume of paste$\equiv V=$about 25 c.c., and 1% potato paste of $\varphi\fallingdotseq 60$. Mark □ shows the variation under such a condition as the frequency of ultrasonic waves$=470$ KH$_z$, the diameter of the plate$=35$ m.m., and input$\equiv W=650$ watts. When frequency was 800 KH$_z$, the quartz plate being 40 m.m. in diameter, and the intensity of irradiation was made to be approximate to that in the case of 470 KH$_z$ with respect to the height of oil fountain in an oil bath, the variation in φ as indicated by mark ○ was larger than that in the former case (mark □) in the graph. A variation similar to that of ○ at 470 KH$_z$ required W$=820$ watts and the variation obtained is indicated by mark △. The influence of frequency must be further investigated, but at least it is seen from the above results that 800 KH$_z$ is effective rather than 470 KH$_z$.

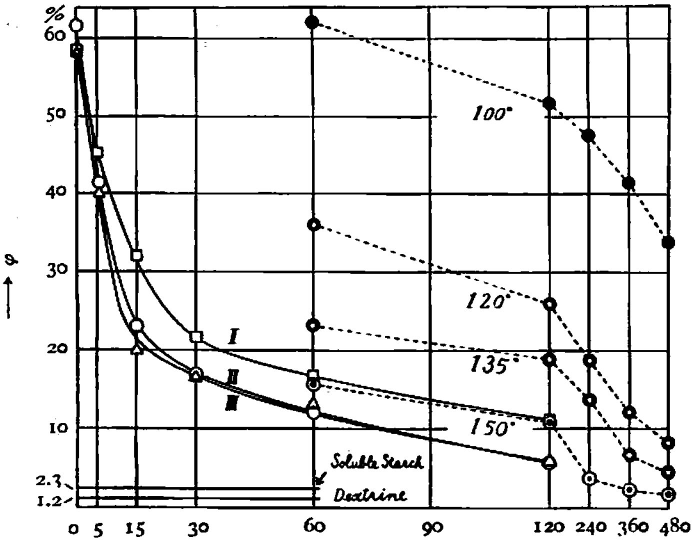

Fig. 3—Disintegration curve of 1% potato paste.

The variation of the paste caused by ultrasonic waves was compared with that by heat treatment, the dotted lines in the graph show the reduction of φ values by heat. The φ values were calculated by formula (1) from Samec's observed values of viscosity.[17] Marks ●, O, ◎ & ⊙ denotes 100°C., 120°C., 135°C., and 150°C. respectively. Comparing the real lines with the dotted ones it is seen that the effect to reduce φ of the paste is comparable to the heat treatment at about 150°C. The corresponding temperatures vary, of course, according to the intensity of ultrasonic waves. The φ values of the so-called soluble starch and dextrine are 2.3[18] and 1.2[19] respectively. Under the present author's experimental conditions, even by two hours' irradiation of ultrasonic waves, the φ value was still larger than those values. In all the experiments mentioned below, 800 KH_z was used and the sample used was 1% potato paste unless indicated particularly.

(B) Influence of the temperature of paste.

By varying the temperature of the paste, whether the reduction of φ was affected or not was examined. Under such a condition as temperature $\equiv T = 15° \sim 60°$C., $D = 0$ m.m., and time of irradiation $\equiv t = 15$ minutes, variation in $\Delta\varphi/\varphi$ was merely of a degree comparable with experimenteal error, as shown in Fig. 4.

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[17] M. Samec, "*Kolloidchemie der Stärke*" (1926) p. 262; M. Samec u. F. von Hoeff, *Kolloid Beih.*, 5, 169 (1913).

[18] M. Samec, "*Kolloidchemie der Stärke*" p. 258.

[19] M. Samec, *ibid.*, p. 284.

This shows that the efficiency of disintegration is independent of temperature in the range 15°∼60°C. The dots marked on the graph indicate the mean values of the three observed values, the evaporation of water being corrected.

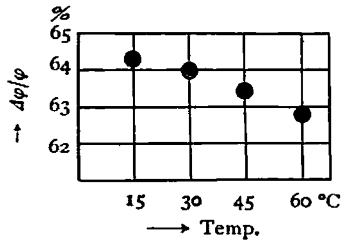

Fig. 4—Influence of the temperature of the paste

(C) Microscopic structure

As above described, η, accordingly φ, is reduced by ultrasonic waves, and in parallel with this a great variation in the shape can be microscopically observed. Fig. 5 (a)∼(j), Plate I∼III, is a series of microphotographs showing variations in 1% potato paste with the time. (a) is the paste not treated by ultrasonic waves. Starch granules are fully swollen and form vesicles, in some of which the interior is flowing out. The vesicle walls (amylopectin) are somewhat expanded by irradiation for 30 seconds and partly broken down; η begins to reduce and accordingly φ does. As time goes on, enlarging of the vesicle walls and their fragmentation advances in parallel: the enlarging process seems to be completed in about 5 minutes. Now let us call this further enlarging of amylopectin already swollen as "super swelling". As time still goes on, the shape becomes smaller, but even after 30 minutes what is shown in (h) remains. Thus, in 2 hours the state shown in (j) is reached.

(D) Wheat paste

As potato was examined as a kind of root starch, so wheat was examined as a kind of cereal starch.

Variation in φ caused by irradiation of ultrasonic waves is almost similar to the case of potato. An instance in a concentration of 1% is graphically shown in Fig. 6 and its microphotographs are shown in Fig. 7, (a)∼(h) Plate III∼V. It must be noted here that in the earlier stage the φ value is rather larger than that of paste before irradiation. This may be because the increase in viscosity by the "super swelling" overcomes the decrease in viscosity by the breakdown of vesicle walls. Such a phenomenon, however, is also noticed in potato when φ of paste before irradiation is comparatively small on account of insufficiency of swelling and aging during preparation when concentration is large, as will be described later (cf. 5% curve in Fig. 11). With this exception, the 1% wheat paste breaks down in the same process as the 1% potato paste does. In 5 minutes the disintegration of the starch brings forth a state in which large granules shown in (e) and smaller ones in (e′) mingle: in 15 minutes the state changes as shown in

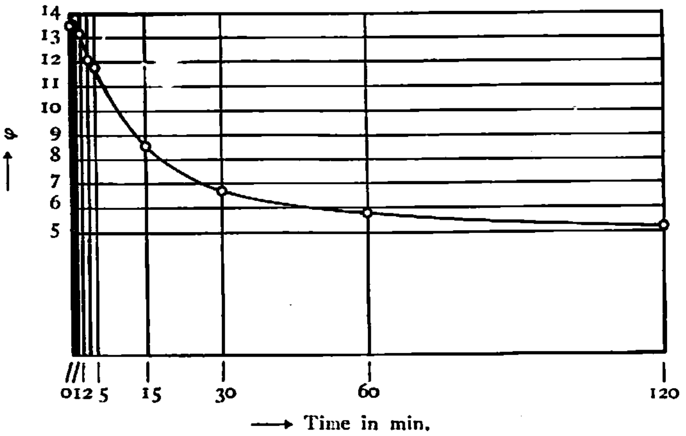

Fig. 6—Disintegration curve of 1% wheat paste.

(f), and in 120 minutes, at last, it reaches such a degree as shown in (h). Comparison of the variation in φ of potato with that of wheat is given in Table III. According to the table, the potato whose φ is originally larger than that of wheat shows larger reduction rate than the latter, but there is hardly any difference between both values of φ after 2 hours' irradiation.

Tabelle III

Comparison between Potato and Wheat

Kinds of Starch	Before Irradiation φ	15 Min. Irradiation		120 Min. Irradiation	
		φ	$\Delta\varphi/\varphi$ (%)	φ	$\Delta\varphi/\varphi$ (%)
Potato	60.0	17.75	55.4	5.3	91.2
Wheat	13.5	8.53	36.8	5.15	59.2

(E) Influence of the external air pressure

The nature of disintegration of the starch paste by ultrasonic waves has been described, and now the mechanism of the disintegration must be considered. For the first step, the influence of the external air pressure was observed. In Fig. 8 $\Delta\varphi/\varphi$ of the potato paste is plotted against the external air pressure. The values on the ordinate will be hereafter called the value of "disintegration effect" or only "effect". Curve I was obtained under the condition: input$\equiv W=$ 670 watts, $D=2$ m.m., and reaction vessel $\equiv R=C_1$; and Curve II: $W=500$ watts, $D=70$ m.m., and $R=C_2$. Time of irradiation was 15 minutes and volume of paste$\equiv V$ was about 35 c.c. for both. As is clear from the graph, the disintegration effect is, roughly speaking, at its maximum under about a pressure of 1 atmosphere and falls at a pressure either higher or lower. Let us see the effect at the side lower than a pressure of 1 atmosphere. A little decrease in the air pressure hardly causes the variation in the effect, but when the pressure is lowered below a certain limit (rapid falling point) the effect immediately starts to decrease and at a further decreased pressure it reaches zero. Although curves I and II have a similar process, the rapid falling point of the former in which intensity is higher deviates towards the lower pressure side than that of the latter, This lower pressure side was investigated more minutely by a series of ultrasonic treatments. The results obtained are shown in Fig. 9. It must be noticed here that the results in Fig. 9 is somewhat different from that in Fig. 8 because potato starch from a different source was used and the mean values of reaction vessels C_1 and C_2 were taken for each observed value.

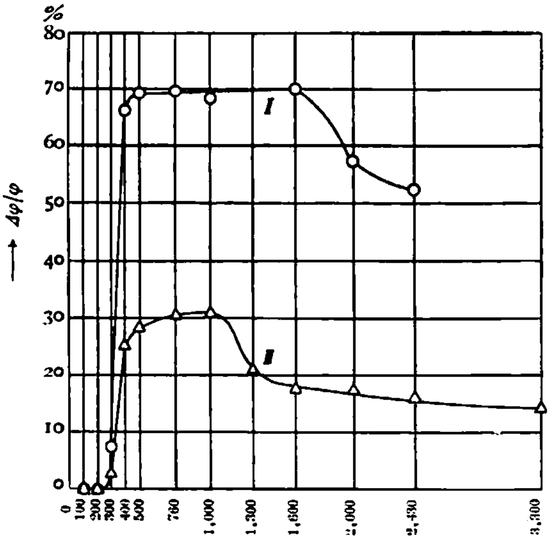

Fig. 8—Influence of external air pressure (Part 1).

Curve I was obtained under the condition: $W=650$ watts, $D=2$ m.m., and $t=15$ minutes; and curve III: $W=620$ watts, $D=70$ m.m., and $t=30$ minutes. In the former the intensity of irradiation is higher and the time of irradiation is half as long as that in the latter, and yet these two curves are almost in agreement.

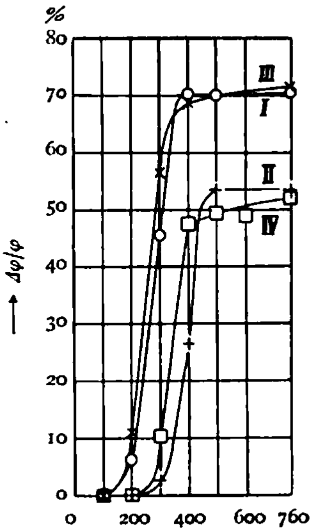

Fig. 9—Influence of external air pressure (Part 2).

Under the condition: $W=500$ watts (smaller than in the case of curve III), $D=70$ m.m., and $t=15$ minutes, curve IV was obtained. By 4 minutes' irradiation, though with the same intensity as in the case of curve I, curve II was obtained: it also approximates to curve IV. By comparing these four curves, it is found that the disintegration effect of starch paste is remarkably influenced not only by the external air pressure, but also by two factors: the intensity of irradiation and the time of irradiation and that, in the present experiments, high intensity and short time of irradiation produces much the same effect as low intensity and long time of irradiation.

In the side higher than 1 atmosphere shown in Fig. 8, curve I indicates that the effect hardly fluctuates until 1,600 Hg. is reached, but when the external air pressure becomes higher the effect gradually begins to decrease. In the case of curve II, the effect varies quite slowly under the pressures greater than 1,000 mm Hg. The item here treated will be detailed later.

(F) Influence of the dissolved gases in paste

Whether or not the disintegration effect is affected by dissolved gases in paste was investigated. About 25 c.c. of paste in a reaction vessel B, air (compressed air), oxygen and hydrogen in bombs were used for this experiment. These gases were passed through two washing bottles holding concentrated sulphuric acid, two bottles holding 33% caustic potash solution, and one bottle holding paste, and flowing out as gas bubbles into the test paste through a hole of about 0.5 m.m. in diameter.

The gases dissolved in paste by a flow of 5 litre per hour was made rich in the flowing gases, and then the flow was stopped, and the effect produced was examined in the atmosphere of the gases. The conditions of irradiation of ultrasonic waves used were $W=$ 550 watts, $D=2$ m.m., and $t=15$ minutes. The result obtained is shown in Fig. 10. A is what was performed in the order of air, oxygen, oxygen, hydrogen, and hydrogen. In B the order is air, oxygen, hydrogen, hydrogen and air. Although the influence of the dissolved gases is extremely little, the effect is larger in oxygen than in air, but smaller in hydrogen than in air.

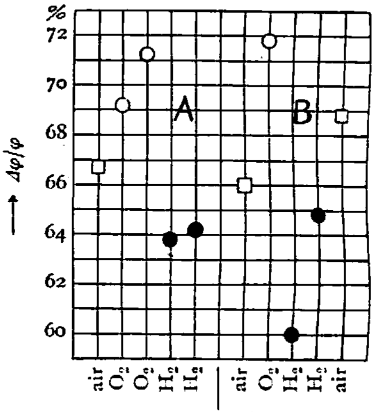

Fig. 10—Influence of dissolved gases.

(G) Influence of the concentration of paste

(i) Disintegration curve (φ-time curve) of 1~5% paste:—Disintegration curves for 1~5% concentration are shown in Fig. 11. With reaction vessel A, the experiment was carried out under the condition: $W=650$ watts, $D=2$ m.m., $V=$about 25 c.c., and $T=30°C$. (only at 5%, $T=60°C$) With reaction vessel B, the effective intensity of ultrasonic waves was higher because the condition of irradiation was the same. The concentration of paste higher than 2% was reduced to 1% after irradiation, and then its viscosity was measured. In the case of a concentration of 1%, φ shows a rapid fall from the beginning, but in 2% a some delay is seen at the earlier stage in the fall of φ, and so is the case with 3%. In 5% the fall of φ is scarcely recognized for 45 minutes. In the earlier stage a somewhat increase in φ is observed. Fig. 12 in the Plate V, is the microphotograph of 5% paste irradiated for 60 minutes. In the case of reaction vessel B with high intensity of ultrasonic waves, such a curve as marked 2% B is formed, where an early delay is scarcely recognized.

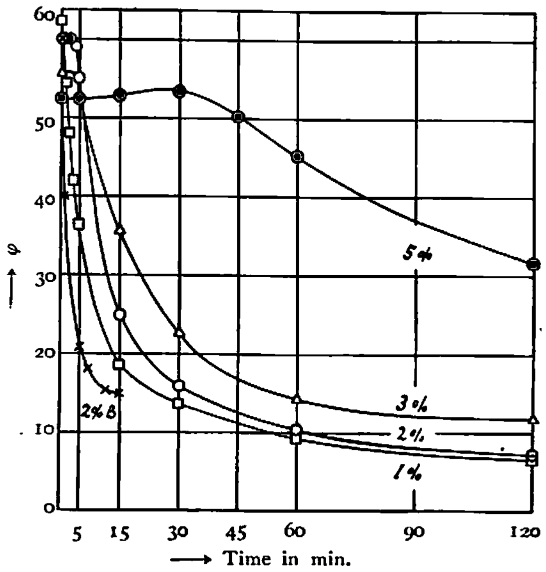

Fig. 11—Disintegration curve of potato paste: Influence of concentration (Part 1).

(ii) Comparison of disintegration effects:—A comparison of the effect, $\Delta\varphi/\varphi$, at various concentrations under 15 minutes' irradiation is shown in curve I of Fig. 13. The curve indicates that in the concentration range 0.1～5% the lower the concentration the larger the effect. Curve I namely shows the mean of variation in each vesicle. If the disintegration of paste is measured as the variation of the apparent volume Φ of the whole vesicles in the same volume of paste, the efficiency reaches a maximum for about 2% as shown in curve II.

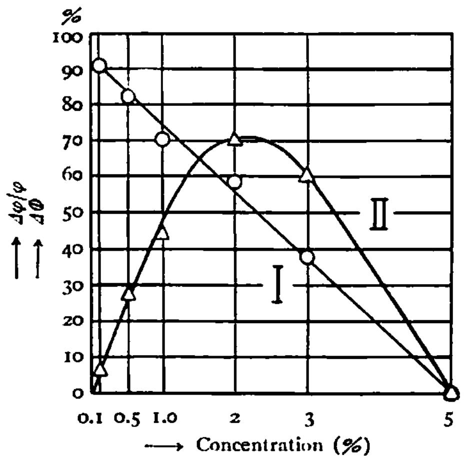

Fig. 13—Influence of concentration (Part 2).

E. Thieme[5] systematically studied the viscosity reduction of solutions of agar-agar, gelatin, and gum arbic caused by ultrasonic waves, and made out that the rate of reduction is at its maximum for a certain critical concentration and that the larger the particles of the above three substances the lower the critical concentration. As to the mechanism of depolymerisation, Thieme's theory is fundamentally the same as Szalay's mentioned in Introduction. In order to explain the influence of concentration, however, Thieme assumed the depolymerisation by collision of large particles and considered the number and efficiency of collision as two factors determining a given critical concentration. Thieme's result that in the part of lower concentration $\Delta\eta/\eta$ is reduced with the decrease of concentration seems apparently contrary to the present author's result, and that it is not really so is clear from the following consideration. By examinning Thieme's report, for example, the experimental value for $0.3 \sim 1.2\%$ gelatine shown in Fig. 7,[5] it is found that Kunitz's formula is also approximately applicable to Thieme's results and φ is $\fallingdotseq 12.0$ as given in Table IV. When the disintegration effect is measured as $\Delta\eta/\eta$, it is true that it decreases, with the decrease of concentration as seen in 8 column of Table IV, but when it is measurd as $\Delta\varphi/\varphi$ it increases with the decrease of concentration as seen in 9 column of Table IV, which agrees with curve I in Fig. 13 drawn by the present author. Regarding $\Delta\Phi$, curve II obtained by the present author is also in agreement with his. It is impossible to observe the variation in shape in the case of Thieme, but possible in the case of the present author. For example, in Fig. 14, Plate VI, (a) is the paste before ultrasonic treatment and (b) is 1% paste irradiated for 15 minutes. As to 0.1% paste, under the same conditions disintegration progresses so much that the particles are entirely imperceptible. Thus the significance implied by $\Delta\varphi/\varphi$ is justified. As mentioned above, it is clear that it explains the fact to regard the disintegration phenomenon as the variation in φ rather than as that in η.

Tabelle IV.

Concentration (%)	Before Irradiation			10 Min. Irradiation			Kinds of expression of rate of disintegration		
	η	Φ	φ	η	Φ	φ	$\Delta\eta/\eta$	$\Delta\varphi/\varphi$	$\Delta\Phi$
0.3	1.17	3.6	12.0	1.11	2.65	8.83	4.27	26.4	0.95
0.6	1.37	6.7	11.2	1.28	5.5	9.2	5.88	17.8	1.2
0.9	1.95	10.75	11.9	1.51	8.8	9.8	8.42	17.6	1.95
1.2	2.12	15.6	13.0	1.88	13.15	11.3	9.95	12.4	2.45
		Mean = 12.0							

(iii) Characteristics of disintegration of 0.1% paste, and its comparison with that of 1% paste :

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[5] E. Thieme, lot. cit.

(a) Fig. 16, Plate VIII is a series of microphotographs* showing an example of disintegration of 0.1% paste under the condition: input$\equiv W=470$ watts, $D=2$ m.m., and $R=C_3$, $V=$about 35 c.c.

The disintegration of 0.1% paste is characterized by the fact that the particles merely become smaller from the beginning and that the super swollen vesicle walls are not recognized on the way to disintegration even if the intensity of irradiation of ultrasonic waves is considerably reduced.

(b) The external air pressure, as shown in Fig. 17,** causes remarkable variation in the effect of 0.1% paste as in 1% paste, but the falling point of the effect deviates to a higher part in the higher air pressure part and to a lower part in the lower air pressure part as compared with that of 1% paste.

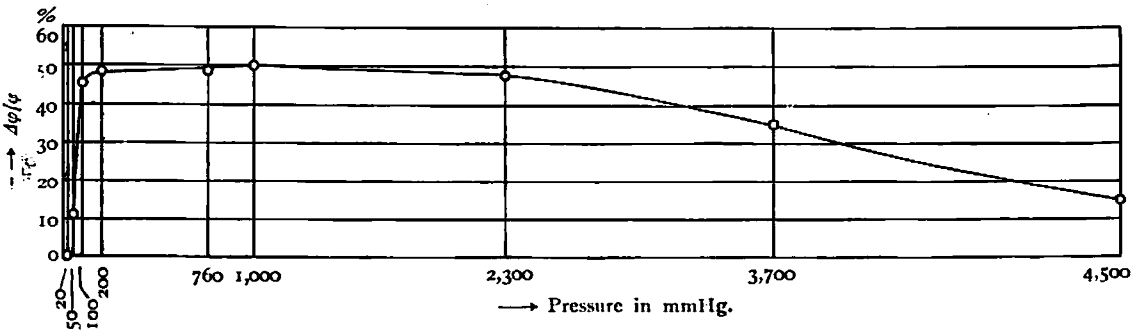

Fig. 17—Influence of external air pressure (Part 3)

(c) As already described, the disintegration effect is markedly greater in 0.1% paste than in 1% paste

IV. Consideration of the experimental results and the mechanism of disintegration

From the experimental results above described, let us consider the mechanism of disintegration of paste granules. First for convenience, let us classify the main factors as follows:

Table V.

I. Mechanical	(a)	Mechanical power through the agency of bubbles (cavities) caused by cavitation or by pulsation of effective bubbles	①
	(b)	Pure mechanical force caused by the vibration of medium particles. (Frictional force)	②
II. Thermal	(a)	Heat generation caused by adiabatic compression of gases occurring in the presence of mechanism ①	③

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* The paste, being placed in a cataphoresis cell, was photographed.

** The experimental conditions; $W=420$ watts, $D=70$ mm., $R=C_3$, $t=15$ minutes, $V=35$ c.c.

	(b)	Addition of kinetic energy of paste granules forced to move by oriented vibration of medium particles.	④
III. Chemical		Depolymerisation accompanied by oxidation by dissolved oxygen in the presence of mechanism ①	⑤

From the above experimental results, the disintegration of paste can be explained thus: the disintegration is chiefly attributed to ① in Table V, the mechanical force through the bubbles (cavities) caused by cavitation or by pulsation of effective bubbles. First, let us refer to Fig. 8 showing the influence of the external air pressure upon disintegration of 1% potato paste. At about 1 atmosphere minute bubbles are seen, with the naked eye, to be generated in the whole paste and disintegration is advancing rapidly. However, a pressure lower than a definite pressure is favourable to formation of cavity and unfavourable to its collapse. Mechanical effect may be attributed to the intensity of collapse of cavity rather than that of formation of carity. Accordingly, the effect of cavitation is reduced. Since the bubbles, boiling promptly, escape out of the liquid, the time during which the effective bubbles exist is very short, and, consequently, the pulsation effect also becomes impotent. At last the disintegration effect may be considered to reach zero when the pressure is lowered until a critical pressure which is equal to 200 mm Hg. in the 1% paste. And in the higher pressure part, the effect begins to decrease at more than 1,600 mmHg. in the case of curve I and at more than 1,000 mmHg. in the case of curve II. This may be interpreted by the assumption that the formation of cavity which becomes unfavoured determines the whole effect. The part of the curve obtained in the neighbourhood of 1 atmosphere almost parallel with the abscissa is considered to show that the decrease of the effect by the unfavourableness of the formation of cavity and the increase of that by the favour ableness of collapse cancel each other. Now, let us observe the effect reduced on the high pressure side more minutely. The larger the variation the more transparent the paste, and after 15 minute's irradiation the variation in the paste is large on the upper part and small on the lower. Observing the variarion with the time, it is found that a clear discontinuous surface concerning the rate of transparency goes downwards.* Fig. 14, Plate VI, gives some photographs corresponding to curve I of Fig. 8: (a) is the paste before irradiation, (b) treated under the ordinary air pressure, (c) and (d)

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* The variation seems maximum at the gas-liquid interface. This is the same phenomenon as the liquefaction of thixotropic gels observed by Freundlich and others.[14] It may be considered that the focused reflection of the sound waves at the interface increases the intensity of the very part, and accordingly the intensity of cavitation.

the uppermost part of the paste treated under 2,430 mmHg. and its lower part respectively. Fig. 15, Plate VII, is a series corresponding to curve II of Fig. 8: (a) is what was treated under the ordinary pressure, (b) and (c) the upper half of the paste under 3,300 mmHg. and its lower half respectively. The values for $\Delta\varphi/\varphi$ at the two parts (b) and (c) of the paste are 23.3% and zero, respectively, and that of a mixture of the two is 14.0%, the experimental value on the graph. Namely, under these conditions, the upper half of paste is varied by cavitation or pulsation effect ①, but the lower half is not varied at all. The distance from the upper surface of the paste to the discontinuous surface, if observed after irradiation for a given time, becomes shorter according as the pressure is increased. Therefore, it is readily inferred that when the pressure is further increased, the paste is not, as a whole, varied. As above described, the mechanism of disintegration of paste is explainable as a mechanical action by the agency of bubbles. When such bubbles exist, however, their temperature elevation is brought about by adiabatic compression of gases, and it leads to the occurrence of hydrolysis by heat, and accordingly the separation of this mechanism ③ from the mechanical one ① above mentioned is difficult.

Secondly, how is the difference between the disintegration types in the cases of 0.1% and 1% pastes explained? From the mechanism of disintegration mentioned above the rate of disintegration is inferred to depend upon both the intensity of the action occurring on the interface between the starch vesicle walls and water and the dimension of the interface. In the case of 0.1% paste each vesicle is suspended isolated from its neighbours because freely vibrated water occupies the greater part. On the contrary, in the case of 1%, as Φ is large, the vesicles are in contact with one another and the interface between starch and freely vibrated water is considered to be very small. Therefore, it is supposed that the area on which one vesicle is subjected to the action is far smaller in 1% than in 0.1%. Besides, the intensity of the action on the interface can never be considered to be higher in 1% than in 0.1%. Consequently it is readily explained that the rate of disintegration of the vesicle is smaller in 1% than in 0.1%. Why the super swollen stage is seen in the case of 1% can not sufficiently be explained. Further studies on it are now proceeding.

The two types of disintegration shown in the cases of 1% and 0.1% are general types that are to appear at relatively high and low concentrations. These types may also be expected not only for starch but for other highly polymerised compounds.

Next, let us examine whether any effective mechanism exists or not besides ① and ③ given in Table V.

That the disintegration effect increases according as the concentration between 5%～0.1% decreases is not because hydrolysis by the mechanism ④ which Szalay points out occurs with decrease of concentration. For calculations shows that the inertia of starch granule is so large in the field of ultrasonic waves that the particles are considered to remain almost stationary. Therefore, such a mechanism may be denied till the vesicles are considerably broken into fragments, such as soluble starch. Such being the case, the disintegration mechanism ② by frictional force seems rather possible. At both high and low pressures, however, the disintegration effect is zero. It is, therefore, evident that such a mechanism is quite invalid for earlier variations in the disintegration of paste. But, at such a super swollen stage as shown in Fig. 5-(e) in the Plate II, not only are the vesicles soft but also their dimension is comparable with a half length of the sound wave (about 0.94 m.m.), and it leads to the possibility of this mechanism. According to the latest report of Schmid[8] regarding the polystyrol, the depolymerisation occurs even if either oxygen is excluded or cavitation is stopped under a pressure of 15 atmospheres, and it ceases when its molecular weight becomes 30,000. This proves the fact that the principal valency bond can be cut off even by mechanism ②.

Finally, the influence of dissolved gases will be considered. Starch is depolymerised by oxidation: the presence of oxygen is important in this reaction. Ultrasonic waves (or acoustic waves) generate hydrogen peroxide in water and also accelerate the oxidation.[20] According to Bethe,[21] when water is saturated with hydrogen, hydrogen peroxide is not generated, and when water is saturated with oxygen the yield of hydrogen peroxide is larger than when saturated with air. According to Liu and Wu,[22] the presence of cavitation and oxygen is indispensable in the oxidation reaction, such as the oxidation of a solution of potassium iodide. Taking these experiments into account, it is supposed that the disintegration depends partly, though extremely slightly, upon the depolymerisation accompanied by oxydation.

V. Summary & Conclusion

The disintegration of native starch paste of potato & wheat (especially, of former) caused by ultrasonic waves has been studied by measuring the variation

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20) F. O. Schmidt, C. H. Johnson & A. R. Olson, *J. Am. Chem. Soc.*, **51**, 370 (1929).

21) H. Bethe, *Z. phys. Chem.* [*A*], **163**, 161 (1933).

22) Szu-Ciu Liu & H. Wu, *J. Am. Chem. Soc.*, **56**, 1005 (1934).

in φ, the specific volume of particles, calculated from Kunitz's viscosity formula, and, in addition, from the variation in the microscopic structure. The general characteristics of disintegration is as follows:

(i) The disintegration effect is rather larger at 800 KH_z than at 470 KH_z.

(ii) The reduction of φ is comparable to that caused by the heat treatment at about 150°C.

(iii) The temperature of the paste has little influence in the range 15°~60°C.

(iv) The potato starch, whose φ is originally larger than that of wheat starch, shows larger reduction rate than the latter.

(v) The influence of the external air pressure is remarkable, being at its maximum near 1 atmosphere. Under a little higher or lower pressure the effect begins to decrease and finally reaches zero.

(vi) The influence of dissolved gases is very small. Oxygen makes the disintegration larger, and hydrogen, on the contrary, makes it smaller.

(vii) In the concentration range 0.1~5%, the smaller the concentration is, the larger is the disintegration effect.

(viii) The type of the disintegration in comparatively low concentration is different from that in comparatively high concentration. For example, in the case of 0.1% the shape of starch granule becomes smaller from the beginning, but in the case of 1% a super swollen stage is recognized.

From the above results, the mechanisms of the disintegration are considered to be as follows:

(1) The chief mechanism is the mechanical action ① through the agency of bubbles caused by cavitation or pulsation. At the same time, hydrolysis ③ is very often brought about by heating caused by adiabatic compression of bubbles.

(2) An extremely little depolymerisation accompanied by oxydation ⑤ may occur.

(3) Both mechanical power ② caused by pure sound wave and Szalay's mechanism ④ are impotent at least for earlier stage of disintegration.

In conclusion, the author has great pleasure in expressing his sincere thanks to Prof. S. Horiba for his valuable guidance during the course of this research. He also wishes to acknowledge his indebtedness to Mr. S. Sakabe (The Nippon Cloth Kogyo Kabushiki Kaisha, Kyoto) for a grant-in-aid.

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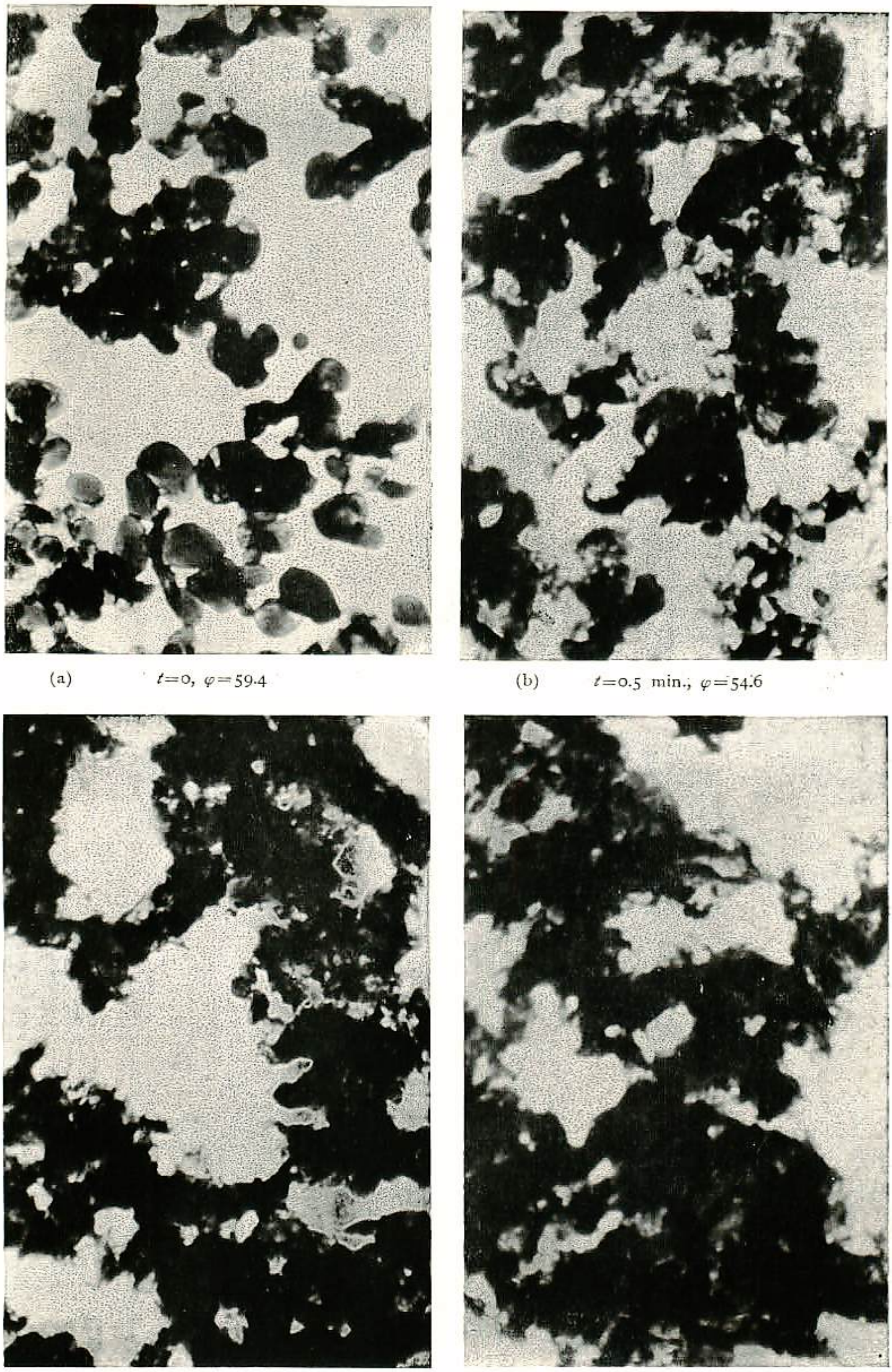


(a) $t=0$, $\varphi=59.4$

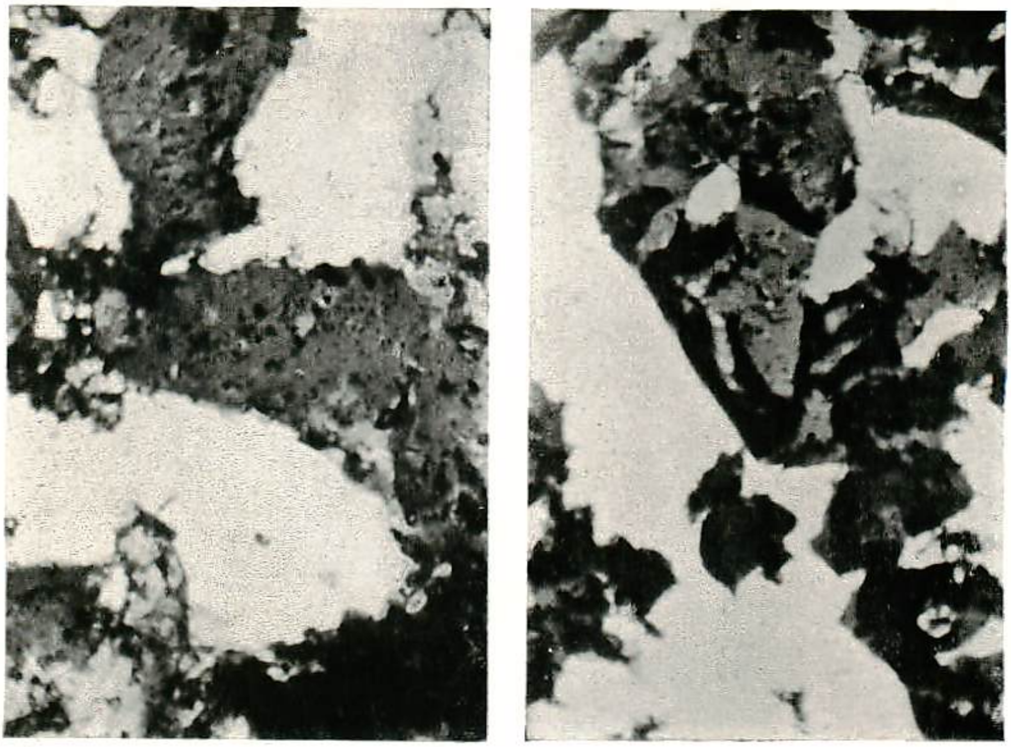
(b) $t=0.5$ min., $\varphi=54.6$

(c) $t=1$ min., $\varphi=47.5$

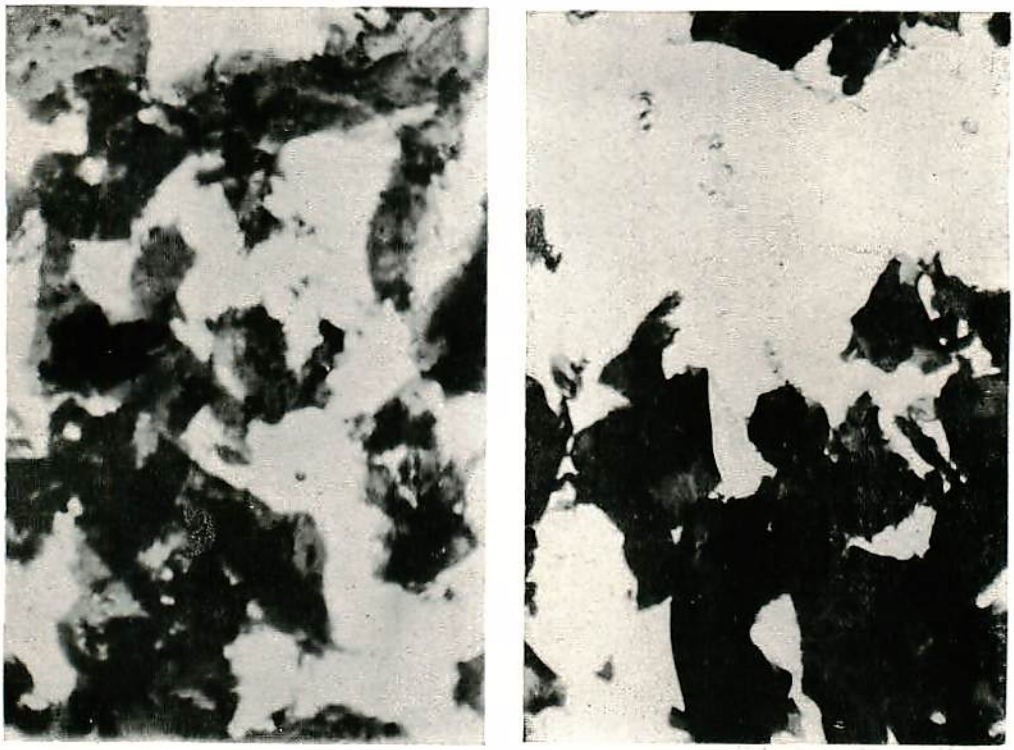
(d) $t=2$ min., $\varphi=42.5$

Fig. 5—Disintegration of 1% potato paste.

(Facing p. 40)

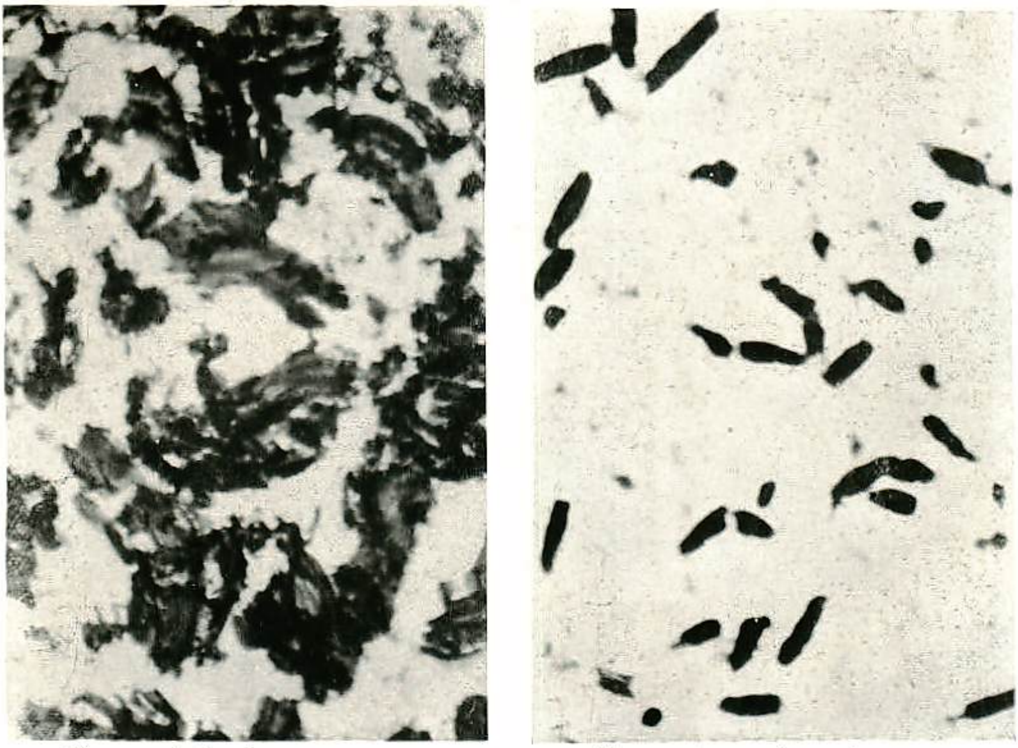


(e) $t=3.5$ min., $\varphi=31.9$ (f) $t=5$ min., $\varphi=28.9$



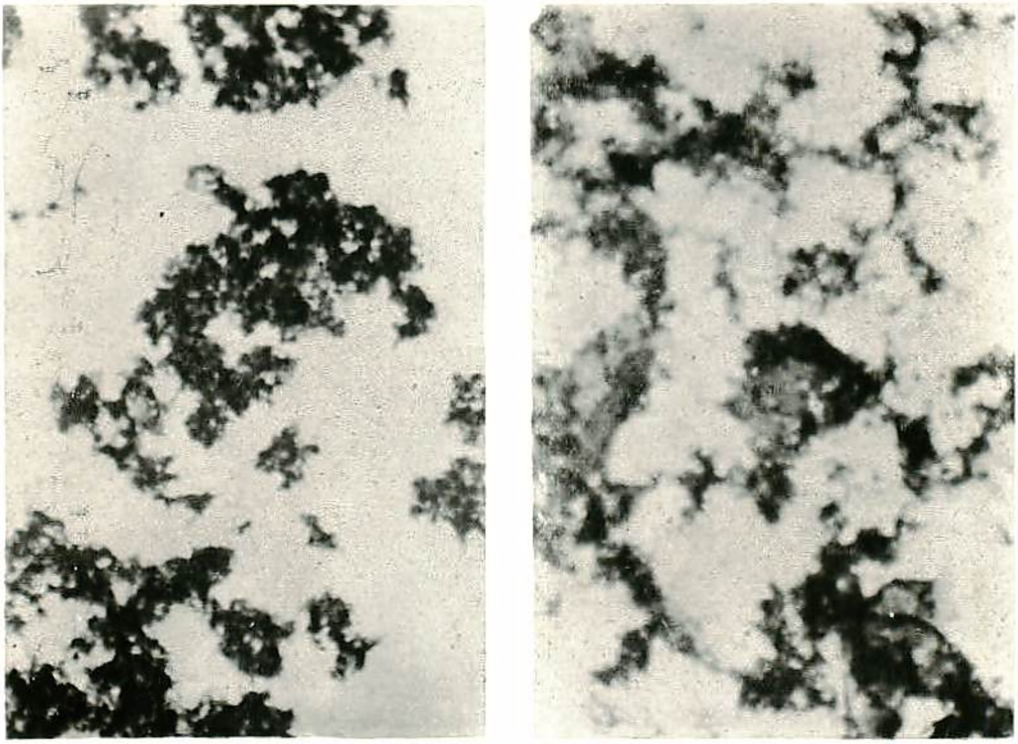
(g) $t=10$ min., $\varphi=25.0$ (h) $t=30$ min., $\varphi=10.1$

Fig. 5—Disintegration of 1% potato paste.—(Continued)



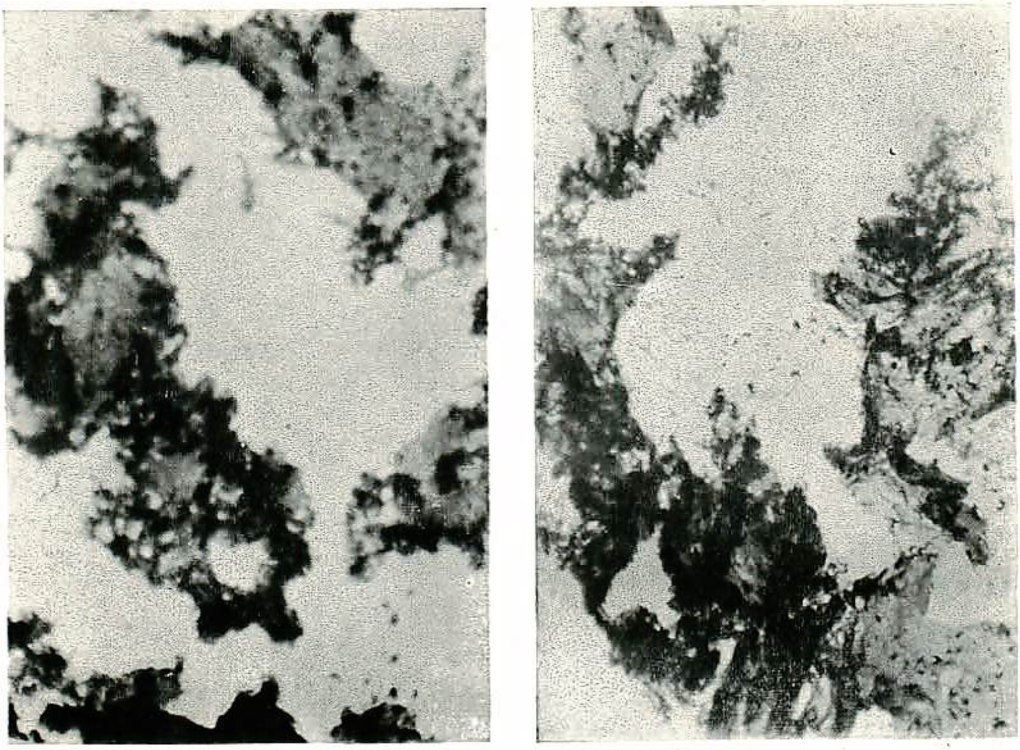
(i) $t=60$ min., $\varphi=9.1$ (j) $t=120$ min., $\varphi=6.4$

Fig. 5—Disintegration of 1% potato paste.—(Concluded)

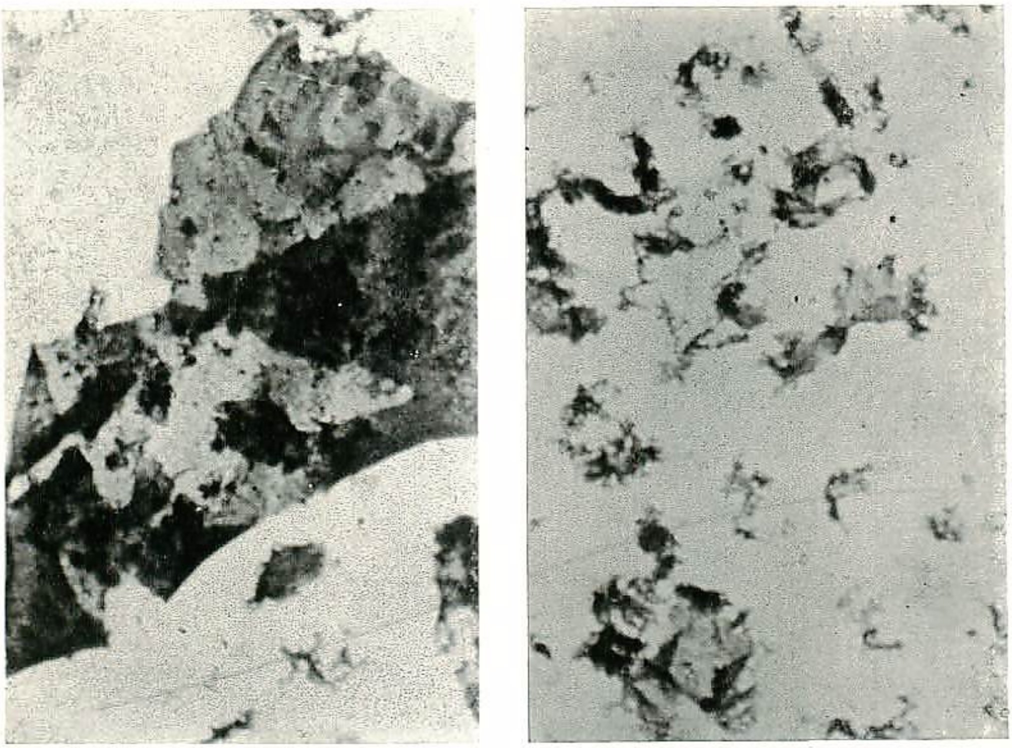


(a) $t=0$ (b) $t=0.5$ min.

Fig. 7—Disintigration of 1% wheat paste,

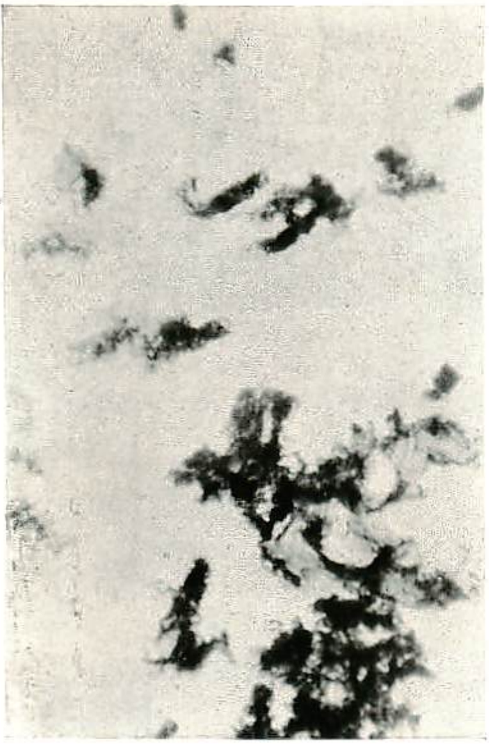


(c) $t=1$ min. (d) $t=3.5$ min.

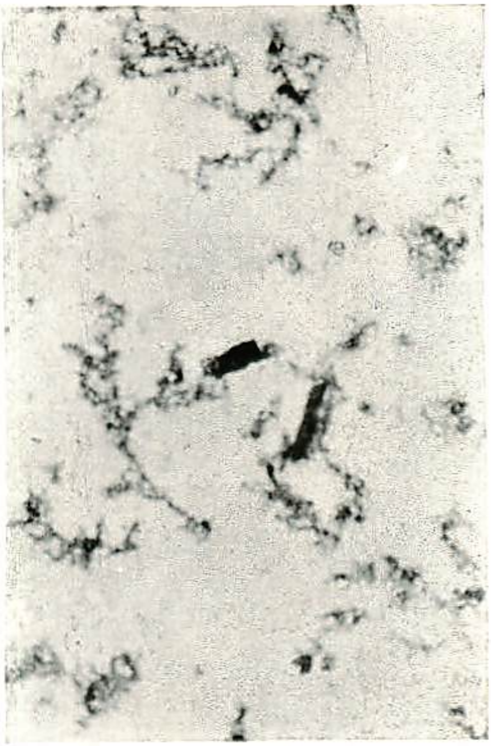


(e) $t=5$ min. (e′) $t=5$ min.

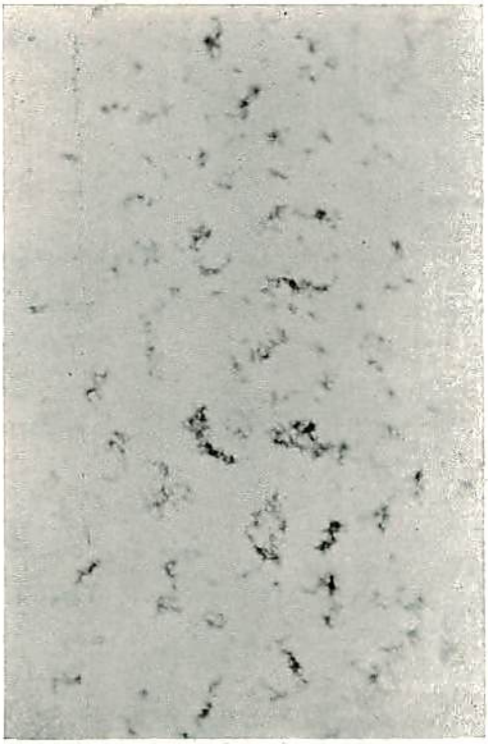
Fig. 7—Disintegration of 1% wheat paste.—(Continued)



(f) t=15 min.



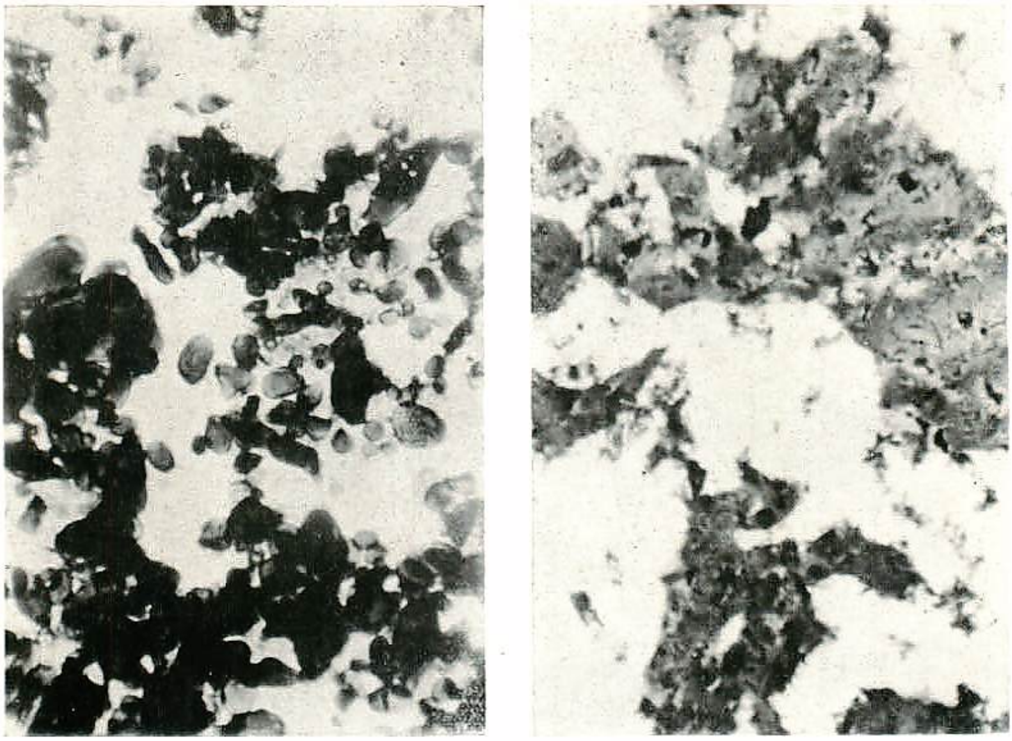
(g) t=60 min.



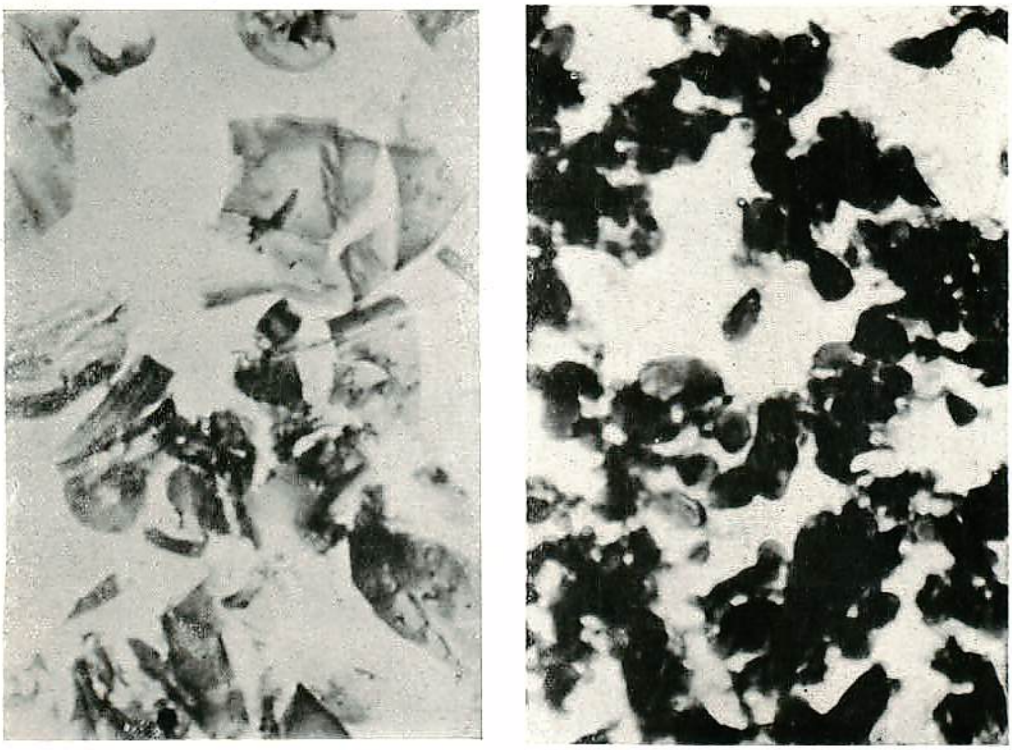
(h) t=120 min.

Fig. 7—Disintegration of 1% wheat paste.—(Concluded)

Fig. 12—Disintegration of 5% potato paste: t=60 min., φ=45.3.



(a) before irradiation (b) p=760 mmHg



(c) p=2,430 mmHg., uppermost part (d) p=2,430 mmHg., lower part

Fig. 14—Influence of external air pressure.

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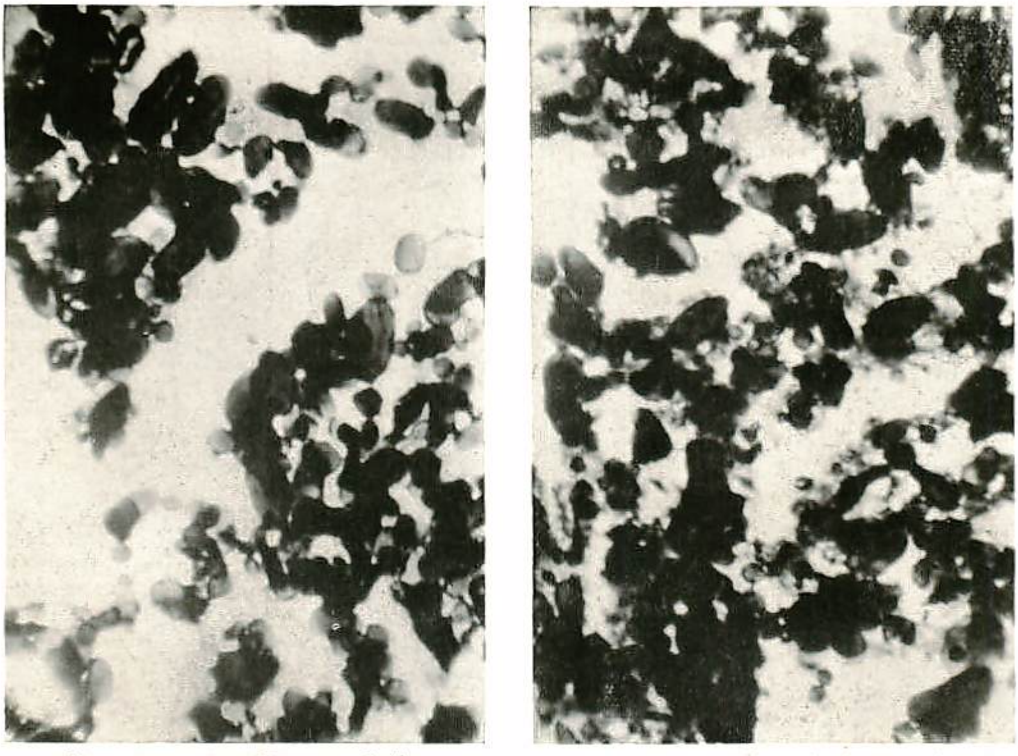
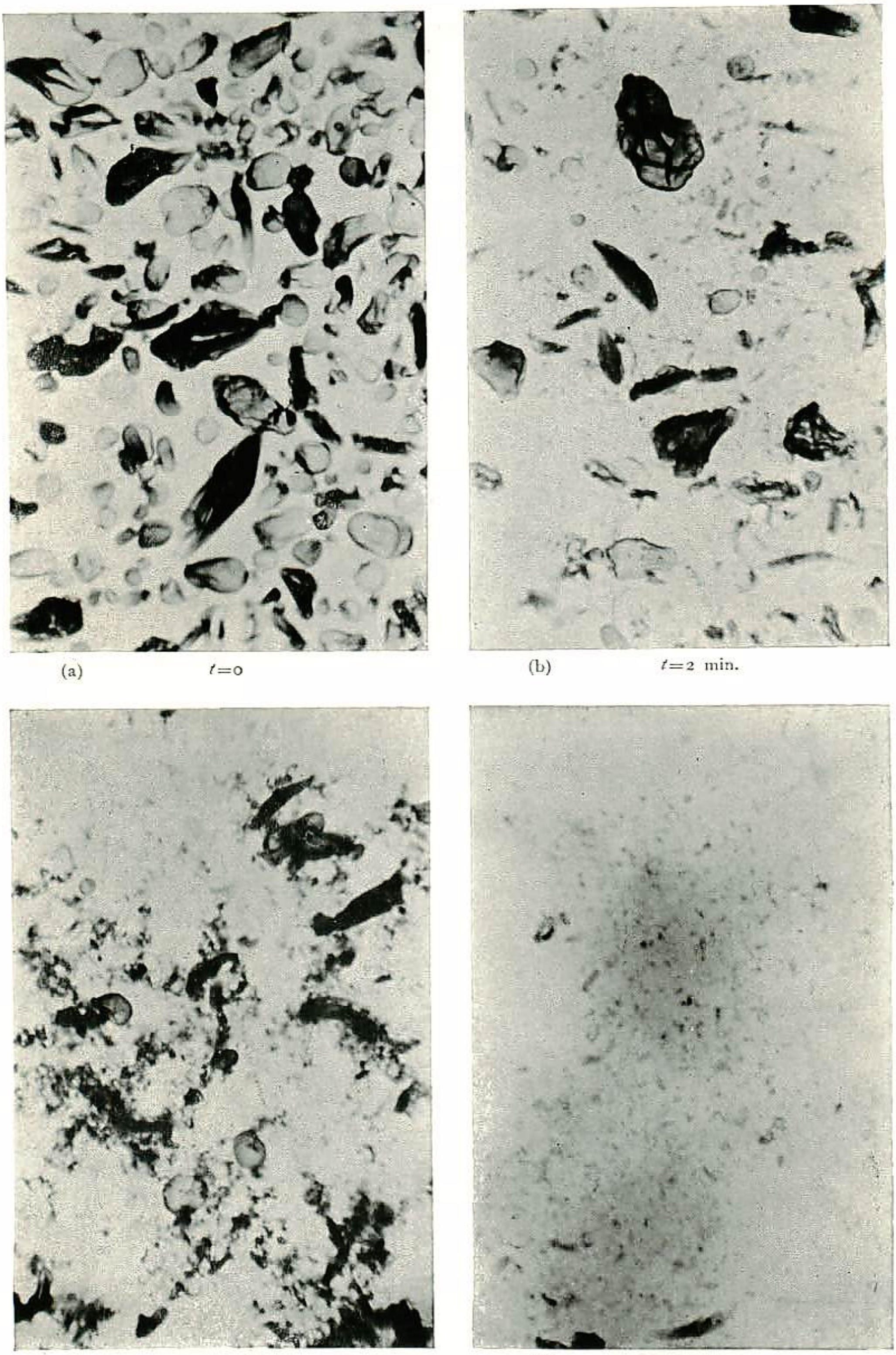
(a) p=760 mmHg



(b) p=3,300 mmHg., upper half (c) p=3,300 mmHg., lower half

Fig. 15—Influence of external air pressure.



(a) $t=0$

(b) $t=2$ min.

(c) $t=5$ min.

(d) $t=10$ min.

Fig. 16—Disintegration of 0.1% potato paste. (placed in a cataphoresis cell)