INVESTIGATION OF THE ETCHING PATTERNS OF SILICIC ACID GELS

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A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry

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INTRODUCTION

It was found that on dissolving silicic acid gels on glass surfaces with strong sodium hydroxide, peculiar etching patterns were formed before the gel dissolved. This observation lead to the study of the etching patterns by photographs and other data for it was believed that these patterns would reveal the structure of the gel.

PROCEDURE

In order to investigate the patterns formed, I prepared acid gels from sodium silicate and a slight excess of acetic acid which set in ten to fifteen minutes, and after a gel had set, enough one normal sodium hydroxide was added to cover the surface. At first I did not observe andy cracks, but instead, the surface turned from clear, transparent to white translucent in a second or two after the base was added.

The next step was to try the same thing on gels an hour or two old. This was more fruitful for on observing the surface, it became covered with very fine cracks which spread over the whole surface very rapidly and then the gel dissolved away.

The time for the first cracks to appear depended on the age of the gel--the older the gel, the longer it took to show signs of cracking.

The next step was to have a number of gels with the same pH or time of set. I did this by preparing a gel mixture and then putting a few drops of the mixture on a number of microscope slides which were put in a dessicator partially filled with water to set, so that the thin films of the gel would not dry out. The films were about .1 mm. thick.

In order to find out whether the process of syneresis had any connection with the etching time of the gels, with the gel mixture that remained, I determined the setting time of the gel films and after the gel had set, weighed it and covered it with water to keep the surface from drying out. From time to time the surface was dried and the gel weighed.

The temperature throughout the experiment was room temperature (about 21°).

Ferromolybdate reagent[1] was used to study the possibility of dying the etching patterns of the gel before applying the sodium hydroxide to the surface. However, the reagent did not make the structure stand out under the microscope, so it was abandoned.

Several series of photographs were taken showing the process of etching on gels of different ages.

1 Chemical Abstracts. XXXIII, 8142[4] (1939).

HISTORICAL

The structure of silicic acid gels gave been under investigation for over forty years but still as little is known today as then of the actual structure. The microscope, ultra microscope, x-ray pattern and absorption spectra have all had their chance, but still the gel structure is unrevealed.

Butschli[2] observed a honey-comb structure under the microscope which he estimated had a cell diameter of 1 or 2μ with a wall thickness of about .3μ. From his observation he outlined the Cellular Theory. Zsigmondy[9] estimated the pore diameter to be about 5mμ for the gel. This size is much to small to be observed with a microscope.

This theory explains the ability for the gel to hold water but does not give any satisfactory explanation for syneresis--the expression of liquid from the gel after setting.

The Fibrillar Theory is the one which is in favor by those working in the field. The solid and liquid phases are continuous with each other, with the solid in the form of a fibrous mesh holding the liquid in its pores. This theory is credited to Nageli[7].

It is well known that sols of silica which have a pH above 11, do not set to form gels. Treadwell and Wieland[8] have formed gels by removing nearly all the sodium hydroxide in a solution of sodium silicate by electrolysis. This brought the pH of the solution below 11.

It is reasonable then by going in the opposite direction--adding sodium hydroxide to a gel--to have the reverse process take place provided enough NaOH is added to bring the pH of the

gel above 11.

This is the process which was observed in etching. If only a small amount of NaOH is added, the etching process occurs, but only a portion of the gel dissolves leaving the pattern on its surface. An excess of NaOH completely dissolves the gel away.

Cormley[5] obtained photographs of these patterns with the belief that they might indicate a possible gel structure. However, the series of photographs which I obtained do not make clear any gel structure.

DATA

The following d ata are on the runs that I made. The age of the gel is taken from the time it set to the time I added the 1. N NaOH. The etching time is the time required to show the first sign of cracking after I put on the base.

Run #1

Setting time, 17 minutes (acid gel)
Weight of gel at start of run, 45.00 gm.

Age of Gel in Hours	Etching time in Minutes	Weight of Gel in Grams
0.00	--	45.00
0.03	.50	--
0.25	.67	--
1.00	.83	44.95
19.7	3.50	43.70
20.0	4.00	--
93.0	7.50-8.25	41.15
113.	--	40.90
142.	--	40.64
167.	--	40.23
262.	15.2-15.8	39.68

Run #2

Setting time, 11 minutes
Weight of Gel at start, 31.82 gm.

Age of Gel in Hours	Etching time in Minutes	Weight of Gel in Grams
0.00	--	31.82
0.17	.62	--
1.00	1.13	--
1.50	--	31.72
4.50	1.95	31.21
20.0	3.50-3.83	30.34
24.0	4.25-4.50	30.22
45.0	5.33-5.75	29.77
121.	10.75-11.25	29.27
140.	--	29.07
169.	13.92-14.50	29.02
189.	--	28.99
289.	--	28.95
337.	--	28.95
361.	30.	28.95

Run #3

Setting time, 12 minutes
Weight at start, 2 6.52 gm.

Age of Gel in Hours	Etching time in Minutes	Weight of Gel in Grams
0.00	--	26.52
0.25	.58	--
1.00	1.06	26.43
2.00	1.35	26.29
17.0	--	25.24
17.5	3.83	--
26.0	3.00	24.90
42.0	5.50	24.57
114.	7.83	24.04
120.	8.55	24.01
167.	10.00	23.91
192.	11.5	23.78
287.	14.3	23.61
335.	*17.2	23.61
359.	*17.0-18.0	23.72
455.	25.0-*29.5	23.72
528.	25.0	23.72
791.	45.0	23.82
1176.	65.0	--
1195.	--	23.94

*These gels were covered with Congo Red to test for cracks before adding the sodium hydroxide. No concentration of the dye was observed to indicate any cracks before etching.

PLATE I

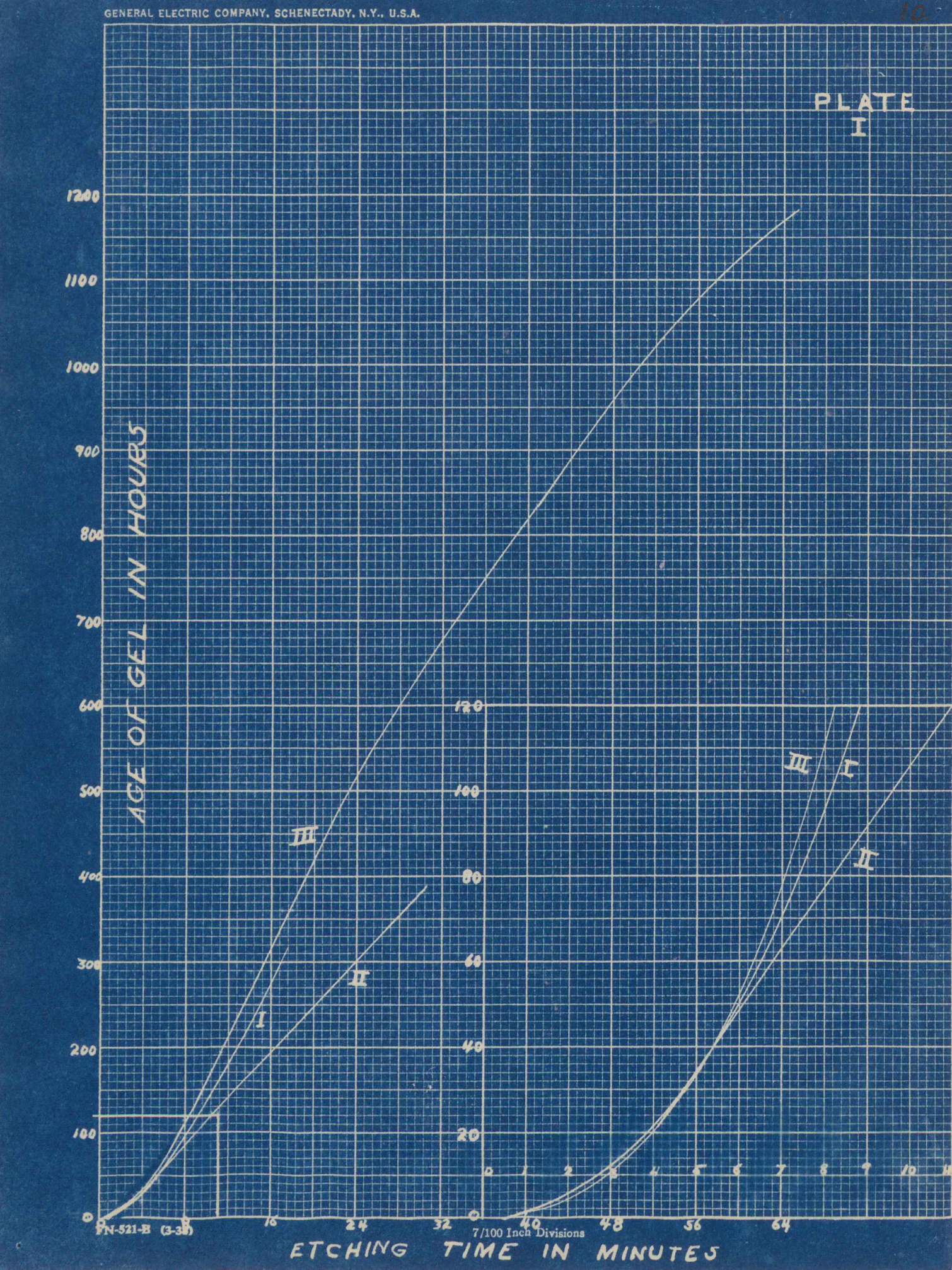

1200
1100
1000
900
800
700
600
500
400
300
200
100
0
AGE OF GEL IN HOURS
I
II
III
120
100
80
60
40
20
0
1
2
3
4
5
6
7
8
9
10
8
16
24
32
40
48
56
64
7/100 Inch Divisions
ETCHING TIME IN MINUTES

PLATE I.

These three curves show the relationship between the age of the gel and the etching time. Curve III shows that the etching time is steadily increasing instead of reaching a limiting value as was expected.

The insert shows the lower portion of the three curves on a larger scale.

Data on Syneresis

Run #1

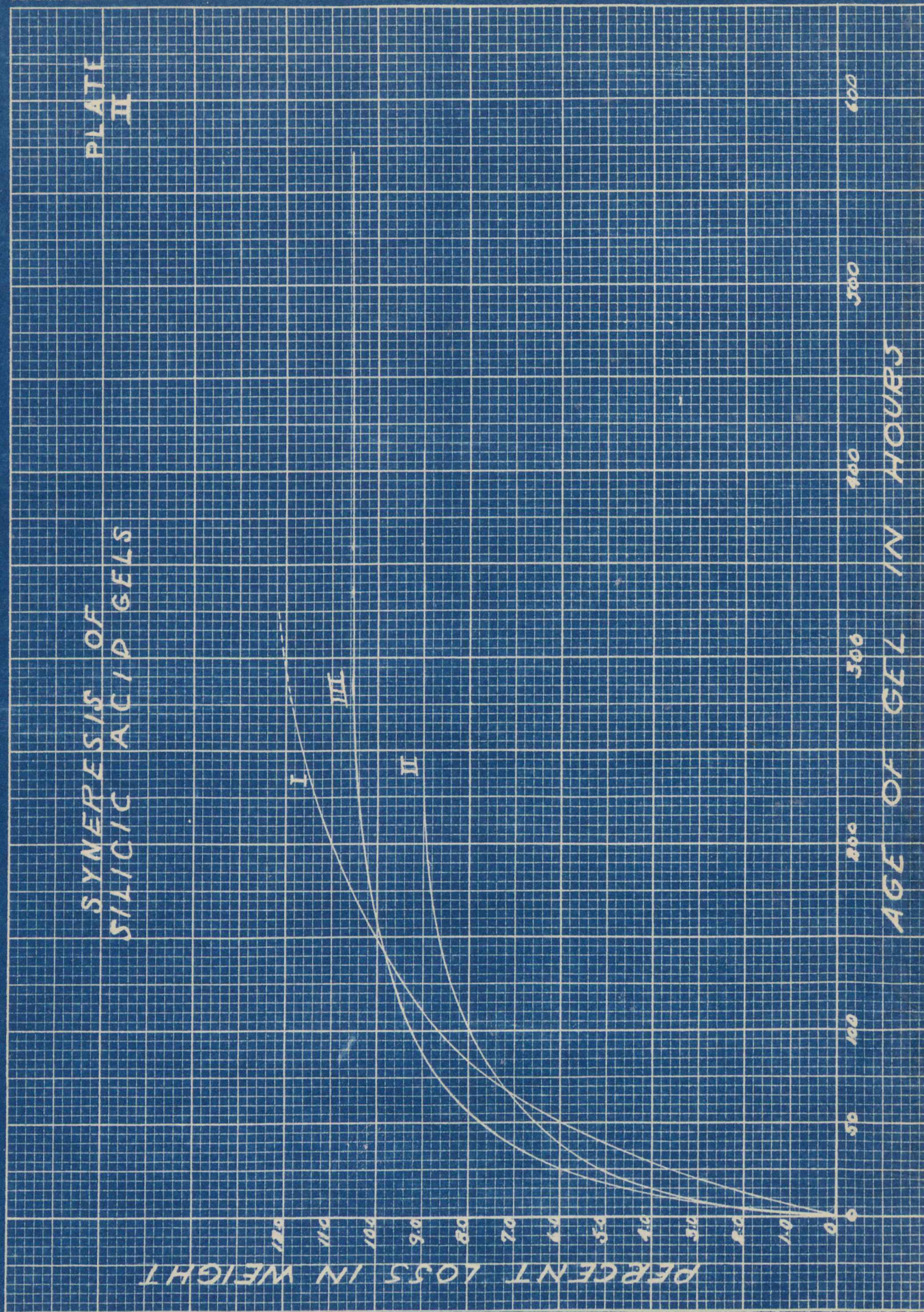
Age of Gel in Hours	Per Cent Loss of Weight
0.00	0.00
1.00	0.11
19.7	2.90
93.0	8.55
113.	9.11
142.	9.69
167.	10.6
262.	11.8

Run #2

Age of Gel in Hours	Per Cent Loss of Weight
0.00	0.00
1.50	0.31
4.50	1.92
20.0	4.65
24.0	5.03
45.0	6.44
121.	8.01
140.	8.64
169.	8.80
189.	8.89
289.	9.02
337.	9.02
361.	9.02

Run #3

Age of Gel in Hours	Per Cent Loss of Weight
0.00	0.00
1.00	0.34
2.00	0.87
17.0	4.90
26.0	6.11
42.0	7.35
114.	9.35
120.	9.47
167.	9.84
192.	10.33
287.	10.56
335.	10.56
359.	10.56
455.	10.56
528.	10.56
791.	10.56
1195.	10.56



7/100 Inch Divisions

PLATE II.

These three curves correspond to the three curves of Plate I. There was insufficient data for curve I to get the limiting value of the loss of weight of the gel. For curves II and III the loss of liquid from the gels reached a limiting value after about twelve days.

DATA ON PHOTOGRAPHS

The exposure time for all pictures was three seconds. The magnification is about two. Illumination was from above and was photographed from above.

SERIES 1.

GEL IS TWO HOURS OLD

First photograph taken 1 minute after putting sodium hydroxide on its surface. The others followed at five second intervals. In the first photograph you see the etching process beginning. The second picture shows the upper surface drawing back and dissolving and exposing a second etched layer. The gel is dissolving very rapidly.

SERIES I

1 2 3

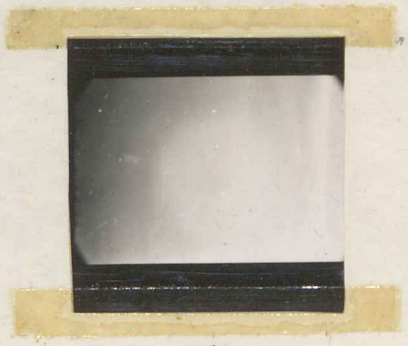
4

SERIES 2.

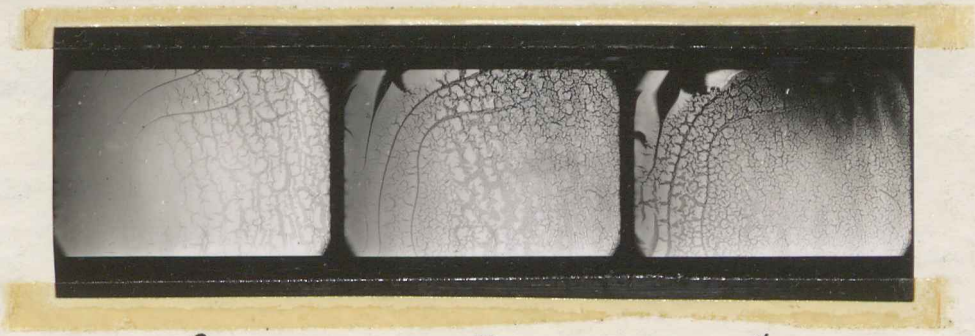
GEL IS THREE HOURS OLD

First photograph was taken 55 seconds after the sodium hydroxide was put on its surface. The other photographs followed at five second intervals. Cracks can just be observed in the first photograph on the right hand edge. These cracks spread very rapidly over the whole surface as is shown in the following photographs.

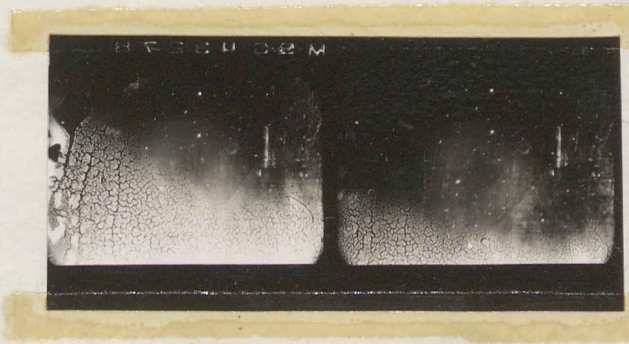
SERIES II



1



2 3 4



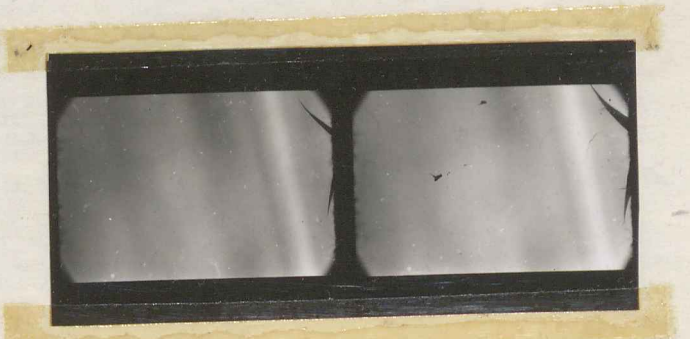
5 6

SERIES 3.

GEL IS SEVEN DAYS OLD

First photograph was taken 8-1/2 minutes after the base was put on its surface. The next 4 followed at 20 second intervals. The last photograph was taken 2 minutes and 40 seconds after the previous one. The slowness of the etching is clearly shown by the time interval between pictures. The cracks are much more coarse than in the first two series. The last picture shows the gel contracting.

SERIES III



1 2

3 4 5

6

SERIES 4.

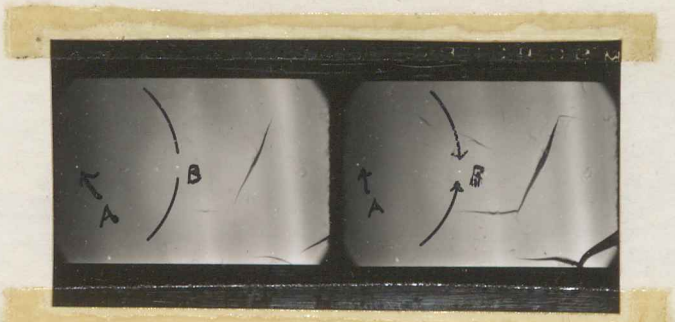
GEL IS FOURTEEN DAYS OLD

First photograph was taken 17-3/4 minutes after the base was put on the surface. The next three followed at 30 second intervals. The last one was taken 2 minutes after the preceeding one.

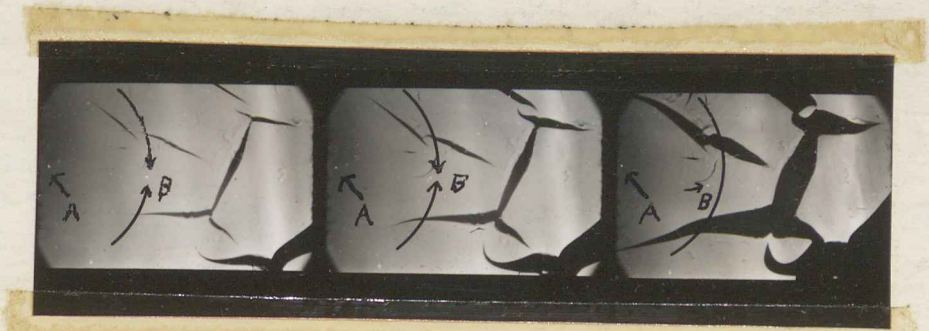
This series is marked to show the movement of the gel surface. Points A and B are on the surface of the gel. As the etching proceeded, the points moved closer together showing a shrinkage of the surface.

The curved lines are arcs of the circle with radius A B of the first picture.

SERIES IV



1 2



3 4 5

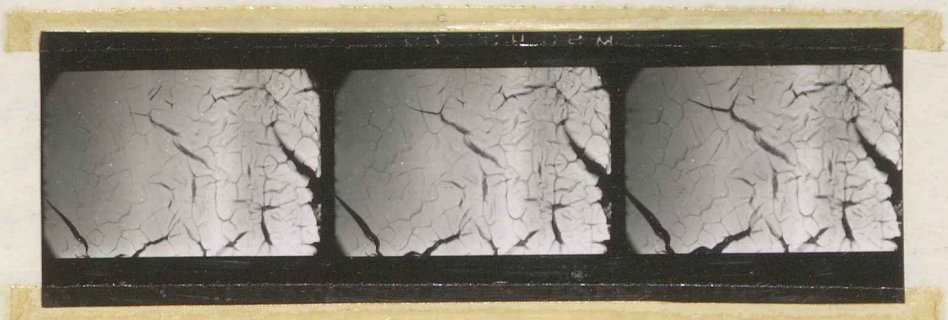
SERIES 5.

GEL IS TWENTY DAYS OLD

First photograph was taken 31 minutes after the base was put on its surface. The next 5 followed at 30 second intervals. The 7th picture was taken 3 minutes after the preceeding one and the last one 3 minutes later.

SERIES V

1 2 3



4 5 6

7 8

RESULTS AND DISCUSSION

The etching process was followed for a long time by observing it under a low power microscope, but this limited the field of view so much that I found it better to observe the gel directly or with a small magnifying glass.

Fresh gels were the best ones to study this process. The first thing observed after putting sodium hydroxide on the gel's surface was a cloudy or milky appearance on the surface. This was soon followed by small depressions forming all over the surface, and connecting forming numerous small cracks. This cracked surface draws back on itself--contracts, and dissolves exposing a new surface to the same process.

The time required for a given series of gels of the same pH and time of set to show signs of etching after NaOH has been added to its surface appears to be a linear function of the age of the gel after the first day for at least a period of twenty to twenty-five days. However, after this time there is a greater increase in the etching time than corresponds to the age. This was rather unexpected for it was believed that the etching time would reach a limiting value with time. Just the opposite appears to be the case at least from this investigation.

The process of syneresis continued for a period of about 12 days with the gels that I studied. After this period, the of the gels remained constant. A study of syneresis was made by Gaunt and Usher[3] and by Boguel.

CONCLUSIONS

1. If there is any relationship between syneresis and the etching time, this has not been revealed in this investigation.

2. A continuous change is taking place in the gel as is indicated by the increase in etching time with age and this change shows no signs of stopping, but rather of increasing. Since x-ray analysis by Krejci and Ott[6] on fresh gels revealed a cristobalite pattern, it may be that a slow process of crystalization is taking place and increasing with time.

3. This investigation revealed that the older the gel, the more coarse the etching pattern formed.

4. The etching patterns are too coarse to show any gel structure.

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