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SIGNED Gordon Hammes

Copies to: Files
Swanson
Hammes

Gordon Hammes

A PRELIMINARY INVESTIGATION OF THE FUNDAMENTAL PROPERTIES OF PITCH AND ITS COMPONENTS

SUMMARY

This report is concerned with the study of the fundamental properties of pitch films in an attempt to discover methods of controlling pitch problems in papermaking.

Four different methods of collecting pitch were attempted.

(1) The collapse of a monomolecular layer of pitch (obtained from an alcohol-benzene extract of groundwood).

(a) Tap water substrate yielded very poor results.

(b) A solution 10^{-6} M in calgon and saturated with thorium chloride yielded 0.0076 grams of pitch after collapsing ten films, and 0.0181 grams after collapsing twenty-five films.

(2) The collapse of a monomolecular layer of pitch formed in a continuous manner by bubbling air through a groundwood pulp solution. The substrate was distilled water 10^{-3} in thorium nitrate and adjusted to a pH of 6.9 with sodium hydroxide. Quantitative film collection was impossible; contamination of the surface film by small pulp fibers was great. A similar experiment using slash pine sawdust as a film source was also unsatisfactory.

(3) Continuous pitch extraction without film collapse.

Air was bubbled through a groundwood pulp solution causing film formation on the surface of a small tray of water. The film ran into an empty flask by means of a piece of filter paper looped over the edge of the tray. This method was too slow and cumbersome to be practical.

(4) Collection of foam. Air was bubbled through a flask containing groundwood pulp. The bubbles were swept into another beaker by means of a stirring rod. Two liters of foam resulted in a residue which contained 0.0974 grams of alcohol soluble material. This method gave a very contaminated foam and filtering was necessary.

Analysis of the pitch collected by foaming gave the following results: 20% rosin acids, 5.13% unsaponifiabiles, 3.4% fatty acid, and insoluble material which tested positive for lignin and weakly positive for carbohydrates.

Analysis of pitch collected by an alcohol-benzene extraction of groundwood pulp gave the following results: 10.5% rosin acids, 22.5% unsaponifiabiles, and 17.2% fatty acids.

Another pitch sample extracted from groundwood with alcohol-benzene and evaporated to dryness was only 78.2% soluble in an alcohol-benzene solution. This indicates polymerization or some similar insolubilizing process occurs during evaporation.

Pressure-area/gram curves were obtained for monolayers of pitch and its fractions by means of a surface balance. Doubly distilled water adjusted to a pH of 3 was used for these studies. The curves obtained contain many kinks. These may be real or may be due to the equipment used. Evidence points to extremely heterogeneous films with peculiar pressure-area curves. Pitch collected by foaming and pitch collected by extraction give different curves indicating different compositions. Extrapolation values (Table XVII) of the straight line portion of the curves for the different pitch types differed greatly.

The deposition of pitch films on step wedges of stearic acid was attempted. The substrate was doubly distilled water containing the following foreign ions: 1.60×10^{-3} in KHCO_3 ; 2.40×10^{-4} in $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$; and 1.58×10^{-5} in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. At pH 6.95 deposition was very poor. When the pH was raised to 8.2 with sodium hydroxide, better deposition occurred. By comparison with a known step wedge, a monomolecular pitch film was found to have approximately the same thickness as that of a stearic acid monolayer ($25 \overset{\circ}{\text{A}}$). Evidence points to the fact that a pitch surface film may have a large gaseous phase.

More experimental work is needed before any general conclusions can be drawn.

INTRODUCTION

Project 1857 was created for the purpose of finding a solution to the problem of pitch control in the paper industry. This problem has faced papermakers for many years, but although many solutions have been suggested, no adequate one has been found.

The basic assumption of this investigation is that pitch exists as a surface film; therefore a study of the properties of this surface film should provide insight into the pitch problem. To gain this end, pitch must be collected and studied as a surface film by various instruments and techniques such as a surface balance and deposition on metal slides.

If our basic assumption is correct, a thorough knowledge of the properties of a pitch surface film should make the solution of the whole pitch problem only a matter of putting together pieces of experimental data.

EXPERIMENTAL WORK AND DISCUSSION

The first problem facing this project was the collection of pitch in large enough quantities so that it could be closely examined. Since the basic assumption underlying this project is that pitch exists as a surface film, only surface active materials should be collected for experimentation. Four different methods of collecting surface active pitch were attempted; none of these methods proved wholly successful.

The method first attempted was the collapsing of the surface film in a trough filled with water. For preliminary experimentation a plexiglass tray, whose edges were covered with teflon tape, was used. Pitch was obtained from an alcohol-benzene extraction of groundwood pulp. This pitch was spread onto the surface of the water contained in the previously mentioned tray. The film was then collapsed by compressing it from both ends with glass barriers covered with teflon tape. When the film was collapsed in the middle of the tray, it was scooped from the water by a small scoop made of aluminum foil. The substrate first employed was tap water; however this was found to be unsatisfactory. A solution 10^{-6} M in calgon and saturated with thorium chloride was then tried. Because of the high pH of tap water, thorium hydroxide precipitated out of the solution and could be seen in the bottom of the tray. This precipitate was gradually depleted as films were collected indicating that thorium ion was combining with the surface film. Samples were collected and dried in the air for about an hour and a half. A brown sticky residue was found in the following amounts:

(a) Ten film collapses yielded 0.0076 grams.

(b) Twenty five film collapses yielded 0.0181 grams.

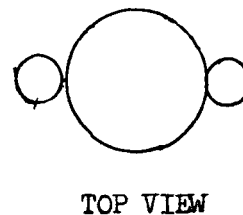
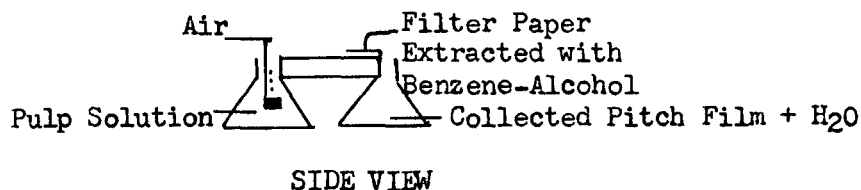
Since one film collapse takes from five to ten minutes this method of collection is obviously too slow to be of practical value.

In order to increase the efficiency of film collection, a larger tray was constructed (1 ft. by 4 ft.). A large flask with a notch in one side was mounted at one end of the tray.



The flask was filled with a pulp solution and air was bubbled through this flask by means of a gas dispersion tube. The pitch, being surface active, attaches itself to the air bubbles and rises to the surface where it spreads a film on the surface of the water in the tray. By use of this method, film formation is continuous. The collapsing and collecting of pitch films, therefore, should be very rapid. The substrate used in this experiment was a distilled water solution 10^{-3} M in thorium nitrate adjusted to a pH of 6.9 with sodium hydroxide. Using a two per cent solution of groundwood pulp as a source of pitch, film collection was attempted. Two difficulties immediately arose: film collapse was not very good; and small fibers came over from the flask and contaminated the film. A screen was put over the slot to control the latter difficulty, but it was not very effective. In order to obtain an uncontaminated film, a two per cent solution of slashed pine sawdust was put into the flask. This also proved unsuccessful because of tiny contaminating fibers present and poor film collapse.

The following apparatus was used in an attempt at a method of continuous pitch extraction.



Pitch film forms on the tray as in the previous experimental setup, but the film is carried to another flask by means of a piece of filter paper. This method of pitch collection proved impractical because of the large amount of water carried over with the film and because of the slowness of the process.

The collection of pitch as a surface film appeared to be impossible; therefore a foaming technique was employed to collect all surface active materials present in the pulp. A pulp solution was put into a large beaker, and air was bubbled through the solution by means of a gas dispersion tube. The bubbles that formed on the surface were swept into another beaker by means of a glass rod. In preliminary experimentation, the concentrated foam solution was evaporated to dryness, and, as a purification procedure, ether extractions were made of the residue. The results were as follows:

- (1) 25 cc. of foam yielded 0.0027 g. of pitch
- (2) 125 cc. of foam yielded 0.0141 g. of pitch

Two liters of the foam were collected and filtered. The resulting solution was evaporated to dryness in a vacuum at 40°C. Two extractions were performed on the residue. An ethyl alcohol extraction yielded a residue of 0.0974 grams when evaporated to dryness, while a benzene extraction immediately following the alcohol extraction yielded a residue of 0.0125 grams when evaporated to dryness. The residue obtained from the alcohol extraction was used as pitch in later studies. The foaming technique of collecting pitch has two major disadvantages: the residue obtained at first is essentially a water extract of the pulp because of the pulp fibers that are swept along with the foam; and the collection of foam is a very lengthy and tedious process.

Before studying the properties of pitch film itself, the pitch was divided into four fractions: rosin acids, unsaponifiables, fatty acids, and insoluble material. The pitch collected by the forementioned foam technique contained 20.0% rosin acids, 5.13% unsaponifiables, and 3.4% fatty acid esters. The remaining insoluble material gave a positive test for lignin and a weak positive test for carbohydrate. Because the foam technique yielded a very small amount of pitch, pitch was also obtained by the extraction of groundwood pulp with a 2:1 alcohol-benzene solution. This extract was evaporated to dryness in a vacuum and separated into fractions. This pitch contained 10.5% rosin acids, 22.5% unsaponifiable,

and 17.2% fatty acids. Another sample of pitch collected in a similar manner was found to be 78.2% soluble in an alcohol-benzene solution. This seems to indicate that during the evaporation procedure oxidation or polymerization occurs resulting in the formation of insoluble materials. All samples of pitch and its fractions were stored in a dessicator under nitrogen to prevent oxidation.

The next step was to study the pressure-area curves of pitch and its fractions by means of a hydrophil balance. In this manner, some of the characteristics of monolayers of pitch and its fractions can be determined. A Cenco hydrophil balance with a steel torsion wire was set up in a trough and calibrated. In preliminary experiments, an aluminum trough coated with paraffin was employed; however this was later replaced by a plexiglass trough whose edges were covered with teflon tape. Preliminary work with pitch (obtained from an alcohol-benzene extract of groundwood pulp) and groundwood pulp itself revealed that their surface monolayers behaved very differently than monolayers of pure substances.

Pitch and its fractions were put into a benzene-alcohol solution. Known amounts of solution were put onto the surface of the water by means of a micropipette. In all cases doubly distilled water lowered to a pH of about 3 with hydrochloric acid was used. The surface film was compressed, expanded and recompressed in all cases. Graphs were made with the pressure being plotted against the area per gram. In the case of rosin acids, a

molecular weight of 302 (**abietic acid**) was assumed, and plots of pressure versus area per molecule were made. Typical data are summarized in Tables I-XVI, while typical graphs are shown in figures 1-10.

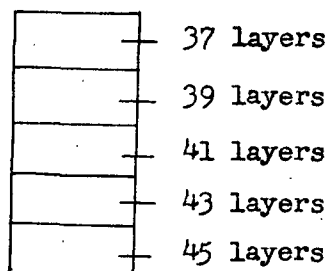
Examination of the graphs shows that all of the curves contain characteristic kinks which indicate phase changes. The kinks are not commonly found in pressure-area curves of pure substances, but they may be due to the heterogeneity of the monolayers of pitch and its fractions. The expansion and recompression curves are probably a function of time. Since no great effort was made at controlling this factor, these curves can be of little significance. Extrapolation of the straight line portion of each curve should give an area per gram (or area per molecule) which is constant for each particular substance. Extrapolation values obtained are summarized in Table XVII. Pure fatty acids give an area per molecule extrapolation value of approximately 20 \AA^2 per molecule; however this value is not valid for heterogeneous films. In the case of pure rosin acids, the extrapolation value is from 40 to 50 \AA^2 per molecule. Once again, however, heterogeneous films do not necessarily give these values.

The data obtained for pitch fractions acquired by foaming are probably less accurate than those obtained for pitch acquired by extraction because of the small weights involved in the former (3-5 mg.). Both types of pitch fractions, however, give different curves indicating that

the composition of these pitch fractions differ. Further data must be obtained in order to gain a thorough understanding of the pressure-area curves of these heterogeneous films.

A preliminary attempt to discover the conditions under which a pitch monolayer will deposit on a metal slide was made. At the same time, it was also possible to approximate the thickness of a pitch monolayer. In order to do this, stearic acid monolayers were deposited on chromium slides. Using the procedure outlined by Blodgett (1), step wedges of stearic acid were made, each step differing by two film thicknesses of stearic acid.

A TYPICAL STEP WEDGE



Each step has a particular color when viewed at a low angle with monochromatic light. By depositing a known number of layers on a stearic acid step wedge, the approximate thickness of the pitch layers can be determined by comparison with a duplicate step wedge with no pitch film deposited on it. A doubly distilled water solution of the following composition was used as substrate for the deposition of pitch film on stearic acid step wedges: 1.60×10^{-3} M in KHCO_3 , 2.40×10^{-4} M in

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, and 1.58×10^{-5} in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Attempts at pitch film deposition were made at two pH's:

- (1) pH 6.95 = Very spotty deposition. Impossible to determine film thickness.
- (2) pH 8.20 = The substrate was made basic by the addition of sodium hydroxide. Film deposition was greatly improved but not to the point of smooth film formation on the slide.

By comparison of the second slide with a step wedge of stearic acid, a pitch monolayer was found to be about the same thickness as a stearic acid monolayer (25 \AA). Because of the fact that the pitch film is very easily compressed and because of the fact that film deposition is not even, one strongly suspects that the pitch monolayer has a large gaseous phase.

This concludes the experimental work accomplished thus far. Only the groundwork has been laid; the largest part of the work lies ahead.

FUTURE WORK

The first problem which must be resolved is how can pitch samples be collected? From the work done thus far, evidence points to the fact that the composition of pitch varies with the method of collection. An alcohol-benzene extraction of wood pulp does not guarantee that all

of the surface active materials have been obtained. Necessity may force the experimenter to go back to film collapse as a means of pitch collection. Possibly the best pitch source would be a hot water extract of wood pulp. This should contain all surface active material present in the pulp. Hand in hand with this problem is the obtaining of an accurate analysis of pitch. Until these problems are mastered, an accurate study of pitch film properties is impossible.

Once a method of pitch collection is found, further surface balance studies are necessary. Improved equipment must be built in order that accurate pressure-area curves can be found. Many of the apparent kinks in the curves obtained thus far may be due to faulty equipment rather than to the surface film. The time required to take a reading on the surface balance must be a constant for all readings. This is especially true of the expansion and recompression curves which appear to be direct functions of time. As soon as accurate pressure-area curves have been obtained for pitch and its fractions, a study of the pure substances should be made for the purpose of comparison, i.e. surface balance studies of abietic acid etc. should be made. The behavior of heterogeneous pitch films will then be more easily understood.

Further attempts at the deposition of pitch films on metal slides is also a necessity. The condition under which smooth films can be deposited should be determined. The film pressure necessary for

film deposition should also be found. This may be the key to the whole pitch problem.

Although much work remains to be done, the basic approach of Project 1857 to the pitch problem appears to be a good one. Through a study of the fundamental properties of pitch films, a solution to the paper industry's age old pitch problem should be only a matter of time.

LITERATURE CITED

1. Blodgett, K. B., J. Am. Chem. Soc., 57, 1007 (1935).

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TABLE I

ROSIN ACIDS OBTAINED BY EXTRACTION OF GROUNDWOOD PULP

TEMPERATURE = 24.8°C.

Compression	Dynes/cm.		Area cm. ²	Area/ Gram x 10 ⁻⁵ cm. ²	Area/ Molecule Å ²
	Expansion	Recompression			
2.07	1.01		345	154	77.2
2.93			318	142	71.2
4.03		1.27	290	129	64.8
5.50	1.27		262	117	58.8
6.84		3.67	234	104.8	52.4
	2.28		221	98.8	49.4
8.69		4.96	207	93.8	46.4
9.52	4.66		193	86.4	43.2
10.1		9.02	179	80.0	40.0
10.7	7.59		166	74.4	37.2
10.8 (5)		10.7	152	67.6	33.9
11.0	10.4		138	61.6	30.9
12.3	11.0	11.7	110	49.6	24.8
13.9			96.6	43.2	21.6
15.9	14.1	16.7	82.8	37.2	18.6
18.2			69.0	30.8	15.4
20.5		21.6	55.2	25.6	12.8

TABLE II
ROSIN ACIDS OBTAINED BY EXTRACTION OF GROUNDWOOD PULP
TEMPERATURE = 24.8°C.

Compression	Dynes/cm.		Area cm. ²	Area/ Gram x 10 ⁻⁵ cm. ²	Area/ Molecule Å ²
	Expansion	Recompression			
2.40			414	148	74.0
2.61			386	138	68.8
3.62			359	128	64.0
4.56			331	118	59.2
5.57			303	108	54.4
6.94			276	98.4	49.2
8.24	0.00		248	88.4	44.4
9.01			221	78.8	39.5
9.21	3.79	5.62	193	68.8	34.4
9.45		8.20	166	59.2	29.6
11.0	8.86	9.11	138	49.2	24.6
12.0			124	44.4	22.2
13.4	9.41	10.7	110	38.4	19.2
14.7			96.6	34.4	17.2
16.2	13.5	16.3	82.8	29.6	14.8
18.8			69.0	24.8	12.4
20.5		20.6	55.2	19.6	9.8

TABLE III

UNSAAPONIFIABLES OBTAINED BY EXTRACTION OF GROUNDWOOD PULP

TEMPERATURE = 25.4°C.

Compression	Dynes/cm. Expansion	Recompression	Area cm. ²	Area/Gram x 10 ⁻⁵ cm. ²
3.36			359	82.6
3.92			331	74.4
5.55			304	69.9
6.17			290	66.7
7.16	0.329		276	63.4
7.66			262	60.3
8.64	0.886	1.44	248	57.1
9.46			234	53.8
10.1	2.18	3.77	221	50.8
10.7	4.51	6.58	193	44.4
13.9	8.03	10.1	166	38.2
16.6			152	34.9
18.8	10.3	11.0	138	31.8
21.0			124	28.5
22.7		18.0	110	25.4
		24.3 (?)	82.8	19.0

TABLE IV
UNSAAPONIFIABLES OBTAINED BY EXTRACTION OF GROUNDWOOD PULP
TEMPERATURE = 26.0°C.

Compression	Dynes/cm.		Area cm. ²	Area/Gram x 10 ⁻⁵ cm. ²
	Expansion	Recompression		
2.66			455	83.7
3.75			414	76.2
4.51	0.00		380	69.9
5.52			359	66.0
7.22			331	60.9
7.77			317	58.3
8.04	1.82	3.98	304	55.9
10.1	3.80	5.65	276	50.7
10.2 (5)			262	48.2
10.4		9.32	248	45.6
10.6 (5)	9.50	10.1 (5)	221	40.7
13.9	10.4 (5)	10.9	193	35.5
16.2			179	32.9
18.3	13.4	15.2	166	30.5
20.5			152	28.0
21.7		21.1	138	25.4

TABLE V

FATTY ACIDS OBTAINED BY EXTRACTION OF GROUNDWOOD PULP

TEMPERATURE = 27.0°C.

Compression	Dynes/cm.		Area cm. ²	Area/ Gram x 10 ⁻⁵ cm. ²
	Expansion	Recompression		
2.73			497	116
3.62			469	110
4.56			442	104
5.74			414	97.2
6.78			380	89.3
8.50			359	84.4
9.99	1.90		331	77.8
11.8 (5)			304	71.4
13.9	7.11	6.83	276	64.8
14.3			248	58.2
16.4 (5)	14.1 (5)	13.9 (5)	221	51.9
19.0	17.0 (5)	14.9	193	45.4
20.3			166	39.0
21.3		21.1	138	32.4

TABLE VI
FATTY ACIDS OBTAINED BY EXTRACTION OF GROUNDWOOD PULP
TEMPERATURE = 27.0°C.

Compression	Dynes/cm.		Area cm. ²	Area/ Gram x 10 ⁻⁵ cm. ²
	Expansion	Recompression		
0.607			525	123
1.52			497	116
2.53			469	110
3.41			442	104
4.48			414	97.2
5.76			380	89.3
6.78			359	84.4
8.73	1.42		331	77.8
10.9			304	71.4
13.1	6.10	6.13	276	64.8
13.6 (5)			248	58.2
16.5	13.4 (5)	12.8	221	51.9
18.4	16.9	14.4	193	45.4
19.4 (5)			166	39.0
20.2 (5)		20.1 (5)	138	32.4

TABLE VII
ROSIN ACIDS OBTAINED BY FOAMING GROUNDWOOD PULP
TEMPERATURE = 27.0°C.

Compression	Dynes/cm.		Area cm. ²	Area/ Gram x 10 ⁻⁵ cm. ²	Area/ Molecule Å ²
	Expansion	Recompression			
1.39			580	74.4	37.2
2.35			525	67.3	33.7
3.87			469	60.2	30.1
5.09			414	53.1	26.6
6.31			380	48.7	24.4
7.04			359	46.0	23.0
8.61	0.00		331	42.4	21.2
9.66			304	39.0	19.5
10.5	2.33	4.02	276	35.4	17.7
10.7			248	31.8	15.9
11.0	7.64	9.72	221	28.4	14.2
11.2 (5)			193	24.8	12.4
12.0	10.9 (5)	11.1 (5)	166	21.3	10.7
13.0			138	17.7	8.86
14.4	12.9	13.5	110	14.2	7.10
16.3			82.8	10.6	5.30
18.3 (5)		18.2	55.2	7.07	3.54

TABLE VIII
ROSIN ACIDS OBTAINED BY FOAMING GROUNDWOOD PULP
TEMPERATURE = 28.2°C.

Compression	Dynes/cm.		Area cm. ²	Area/ Gram x 10 ⁻⁵ cm. ²	Area/ Molecule Å ²
	Expansion	Recompression			
1.74			552	70.7	35.4
3.39			469	60.2	30.1
5.16			414	53.1	26.6
6.27			380	48.7	24.4
6.93			359	46.0	23.0
8.34	0.00		331	42.4	21.2
9.92			304	39.0	19.5
10.7	2.33	4.02	276	35.4	17.7
10.9			248	31.8	15.9
11.1	8.13	9.90	221	28.4	14.2
11.4			193	24.8	12.4
12.3	11.2	11.6	166	21.3	10.7
13.2 (5)			138	17.7	8.86
14.7 (5)	14.1	14.1	110	14.2	7.710
16.8			82.8	10.6	5.30
18.5		18.4	55.2	7.07	3.54

TABLE IX
UNSAAPONIFIABLES OBTAINED BY FOAMING GROUNDWOOD PULP
TEMPERATURE = 28.0°C.

Compression	Dynes/cm. Expansion	Recompression	Area cm. ²	Area/ Gram x 10 ⁻⁵ cm. ²
2.66			359	71.8
4.53			331	66.2
6.56			304	60.8
7.04			290	58.0
8.35			276	55.2
9.35			262	52.4
10.6	0.380		248	49.6
11.3 (5)			234	46.8
11.5	3.24	4.78	221	44.2
11.7 (5)			207	41.4
12.0 (5)	8.18	9.85	193	38.6
13.1			179	35.8
14.2 (5)	11.5	11.6	166	33.2
15.5			152	30.4
16.4 (5)	13.4 (5)	13.4	138	27.6
17.4 (5)			124	24.8
18.5 (5)	17.2	16.8 (5)	110	22.1
19.4			96.6	19.3
20.4		19.2 (5)	82.8	16.6

TABLE X
UNSAAPONIFIABLES OBTAINED BY FOAMING GROUNDWOOD PULP
TEMPERATURE = 27.2°C.

Compression	Dynes/cm.		Area cm. ²	Area/ Gram x 10 ⁻⁵ cm. ²
	Expansion	Recompression		
1.04			386	77.2
2.76			359	71.8
4.53			331	66.2
6.62			304	60.8
8.60	0.683		276	55.2
10.5			248	49.6
12.3	6.47	7.71	221	44.2
12.8	11.9	11.9	193	38.6
13.3			179	35.8
14.2 (5)	12.5 (5)	12.6 (5)	166	33.2
15.6			152	30.4
16.4	14.9	14.8	138	27.6
17.4			124	24.8
18.3	17.7	17.5*	110	22.1
19.4 (5)			96.6	19.3
20.3		18.5*	82.8	16.6

* Apparent loss of surface film.

TABLE XI

FATTY ACID ESTERS OBTAINED BY FOAMING GROUNDWOOD PULP

TEMPERATURE = 27.9°C.

Compression	Dynes/cm.		Area cm. ²	Area/ Gram x 10 ⁻⁵ cm. ²
	Expansion	Recompression		
1.36			414	86.2
2.86			359	74.9
4.86			304	63.3
6.13			276	57.5
7.42			248	51.7
8.79	1.14		221	46.1
9.83			207	43.2
10.3	4.00	4.88	193	46.3
10.7	7.04	8.49	166	34.6
11.5	10.4 (5)	10.5 (5)	138	28.8
13.1			124	25.8
14.5	12.4	12.0	110	23.0
15.4			96.6	20.1
16.3		16.3	82.8	17.3

TABLE XII

FATTY ACID ESTERS OBTAINED BY FOAMING GROUNDWOOD PULP

TEMPERATURE = 28.2°C.

Compression	Dynes/cm. Expansion	Recompression	Area cm. ²	Area/ Gram x 10 ⁻⁵ cm. ²
2.68			497	82.8
3.75			442	73.7
5.24			380	63.3
6.17			359	59.8
7.26	0.962		331	55.2
8.84			304	50.7
9.98	2.96	4.38	276	46.0
11.0	5.32	6.88	248	41.3
11.3		8.76	221	36.8
11.6	10.8	11.0	193	32.2
12.1			179	29.8
13.4 (5)	11.5	11.5	166	27.7
14.3 (5)			152	25.3
15.2 (5)	13.9	13.3*	138	23.0
16.6 (5)		15.8*	110	18.4

*Apparent surface film loss.

TABLE XIII
PITCH OBTAINED BY EXTRACTION OF GROUNDWOOD PULP
TEMPERATURE = 27.3°C.

Compression	Dynes/cm.		Area cm. ²	Area/ Gram x 10 ⁻⁵ cm.
	Expansion	Recompression		
2.00			469	92.3
3.09			442	87.0
4.78			414	81.5
5.55			380	74.8
7.24	0.709		359	70.7
9.40			331	65.2
11.2 (5)	4.68	6.11	304	59.8
11.6			276	54.3
11.8 (5)	10.8	11.2	248	48.8
12.3			221	43.5
13.2	12.4	12.2 (5)	193	38.0
14.3			166	32.7
15.7 (5)	14.7	15.9	138	27.2
17.0	16.5	17.1 (5)	110	21.7
18.5 (5)		18.7	82.8	16.3

TABLE XIV
PITCH OBTAINED BY EXTRACTION OF GROUNDWOOD PULP
TEMPERATURE = 27.8°C.

Compression	Dynes/cm.		Area cm. ²	Area/ Gram x 10 ⁻⁵ cm. ²
	Expansion	Recompression		
1.29			552	87.0
2.43			525	82.7
3.70			497	78.3
4.68			469	73.9
6.02	0.937		442	69.5
7.24			414	65.2
9.00	3.09	3.65	380	59.8
10.7	5.50	6.94	359	56.6
11.8			331	52.2
11.9 (5)	9.86	10.2	304	47.9
12.1 (5)			276	43.5
12.6	12.1 (5)	12.2	248	39.1
14.7			221	34.9
16.0	14.8	14.4	193	30.4
17.2 (5)			166	26.1
17.9 (5)	17.3	17.8 (5)	138	21.7
19.0		19.0	110	17.4

TABLE XV
PITCH OBTAINED BY EXTRACTION OF GROUNDWOOD PULP
TEMPERATURE = 28.1°C.

Compression	Dynes/cm. Expansion	Recompression	Area cm. ²	Area/ Gram x 10 ⁻⁵ cm. ²
2.15			580	91.4
2.99			552	87.0
3.90			525	82.7
4.96			497	78.3
6.03	1.95		469	73.9
6.69			442	69.5
	4.43	4.96	414	65.2
6.96			380	59.8
7.55	6.50	6.81	359	56.6
9.09			331	52.2
10.7	8.13	8.40	304	47.9
11.6			276	43.5
12.7	11.7 (5)	12.6	248	39.1
13.7 (5)			221	34.9
15.0	14.3 (5)	15.7	193	30.4
16.6			166	26.1
18.3 (5)		18.5	138	21.7

TABLE XVI

PITCH OBTAINED BY EXTRACTION OF GROUNDWOOD PULP

TEMPERATURE = 28.2°C.

Compression	Dynes/cm.		Area cm. ²	Area/ Gram $\times 10^{-5}$ cm. ²
	Expansion	Recompression		
2.15			580	91.4
3.90			525	82.7
6.13	2.08		469	73.9
6.98	4.96	5.19	414	65.2
8.86*	6.68	6.86	359	56.6
9.52			331	52.2
10.8	9.35	9.73	304	47.9
11.6 (5)			276	43.5
12.7 (5)	10.7	13.0	248	39.1
13.7			221	34.9
14.7	14.0	15.2 (5)	193	30.4
16.0			166	26.1
17.7		18.2	138	21.7

*Transition point missed.

TABLE XVII

Table Number	Substance	Method of Collection	Extrapolation Value Area/ Gram $\times 10^{-5}$ cm. ²	Area/ Molecule \AA^2
I	Rosin Acids	Extraction	77.2	40.2
II	Rosin Acids	Extraction	71.2	37.8
III	Unsaponifiabiles	Extraction	57.0	
IV	Unsaponifiabiles	Extraction	56.4	
V	Fatty Acids	Extraction	91.0	
VI	Fatty Acids	Extraction	91.5	
VII	Rosin Acids	Foaming	41.8	20.1
VIII	Rosin Acids	Foaming	41.5	20.6
IX	Unsaponifiabiles	Foaming	76.1	
X	Unsaponifiabiles	Foaming	75.9	
XI	Fatty Acid Esters	Foaming	49.0	
XII	Fatty Acid Esters	Foaming	47.2	
XIII	Pitch	Extraction	87.6	
XIV	Pitch	Extraction	85.5	
XV	Pitch	Extraction	Extrapolation Impossible	
XVI	Pitch	Extraction	Extrapolation Impossible	

ROSIN ACIDS (EXTRACTION)

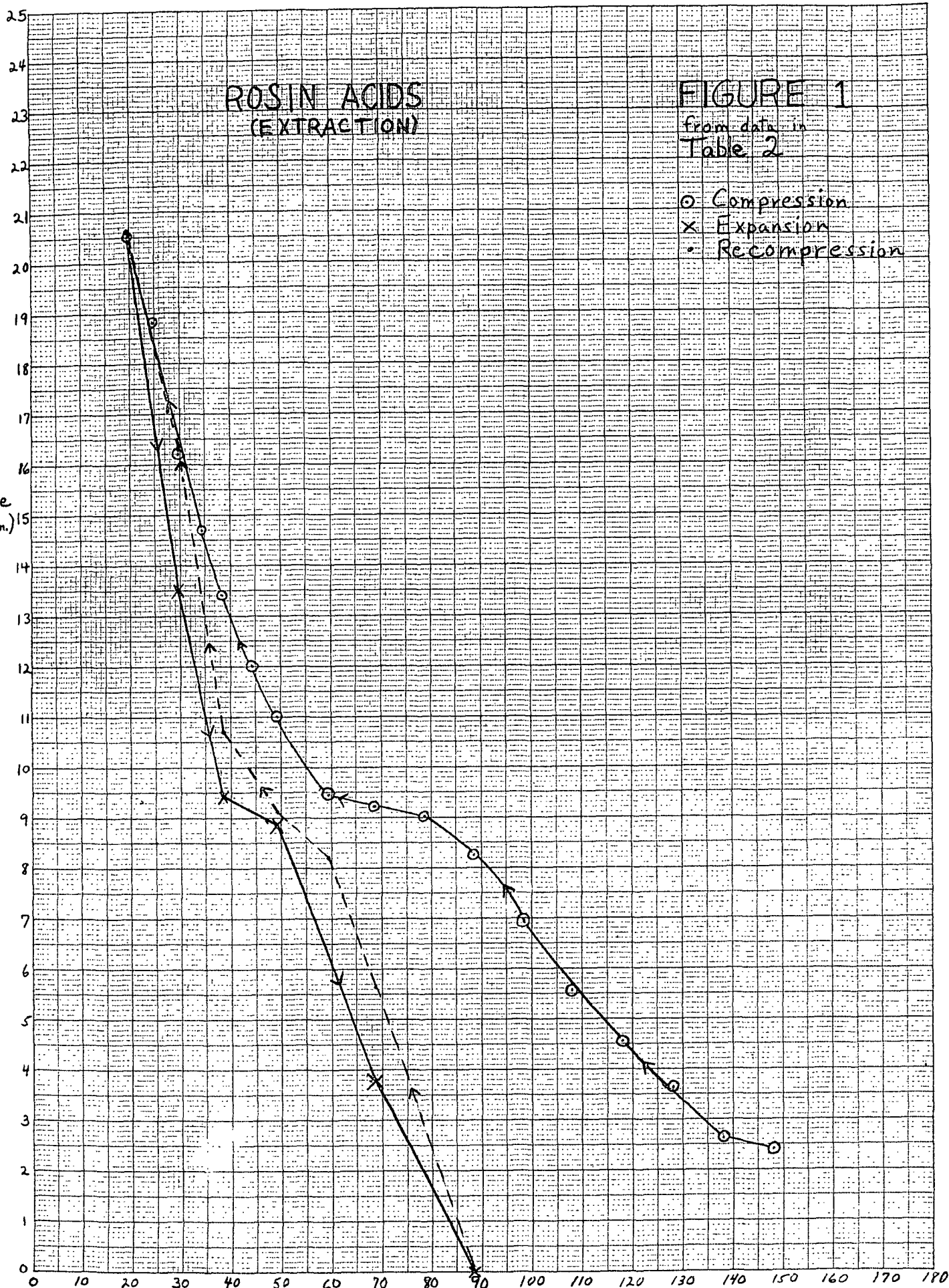
FIGURE 1

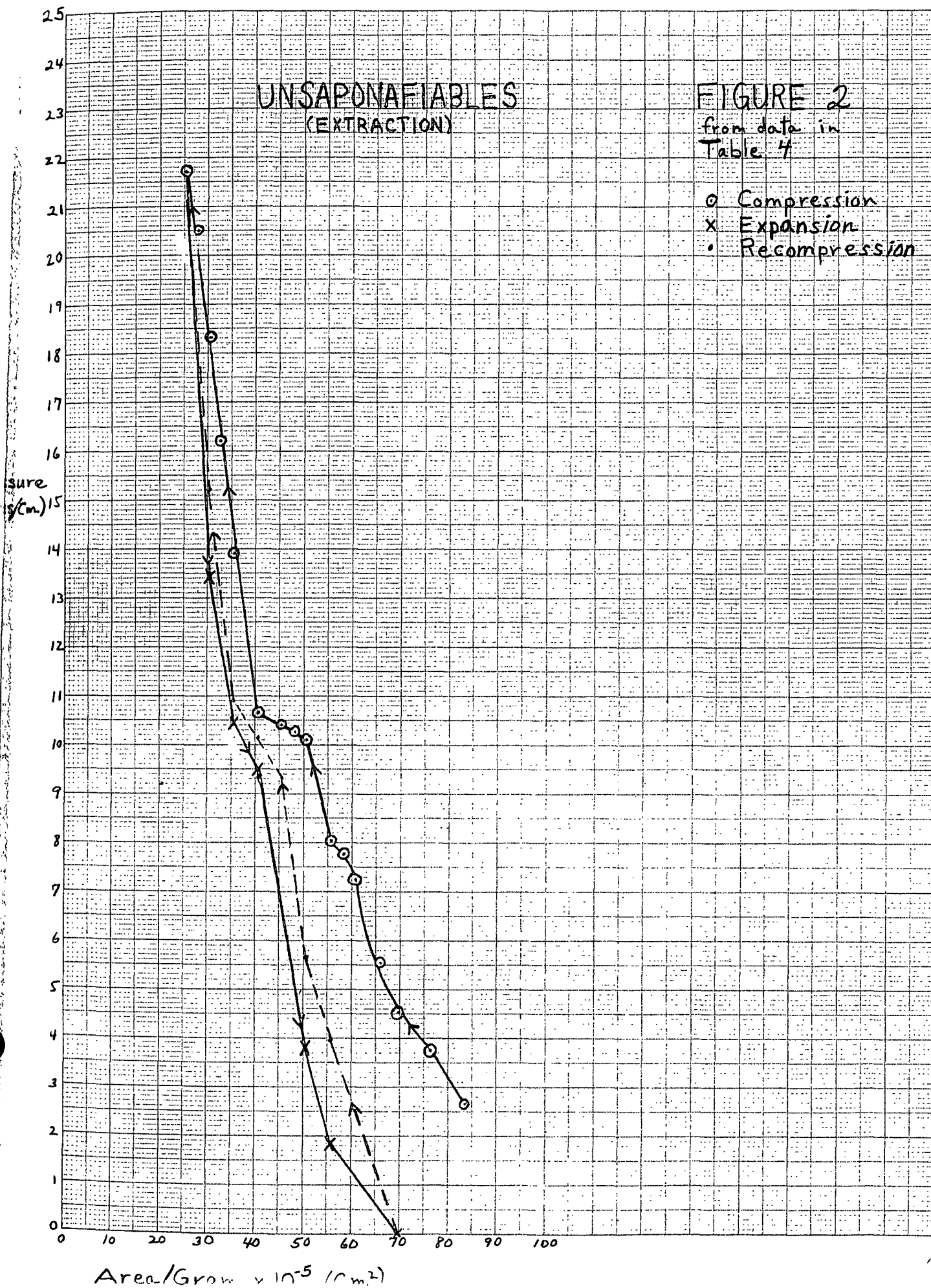
from data in
Table 2

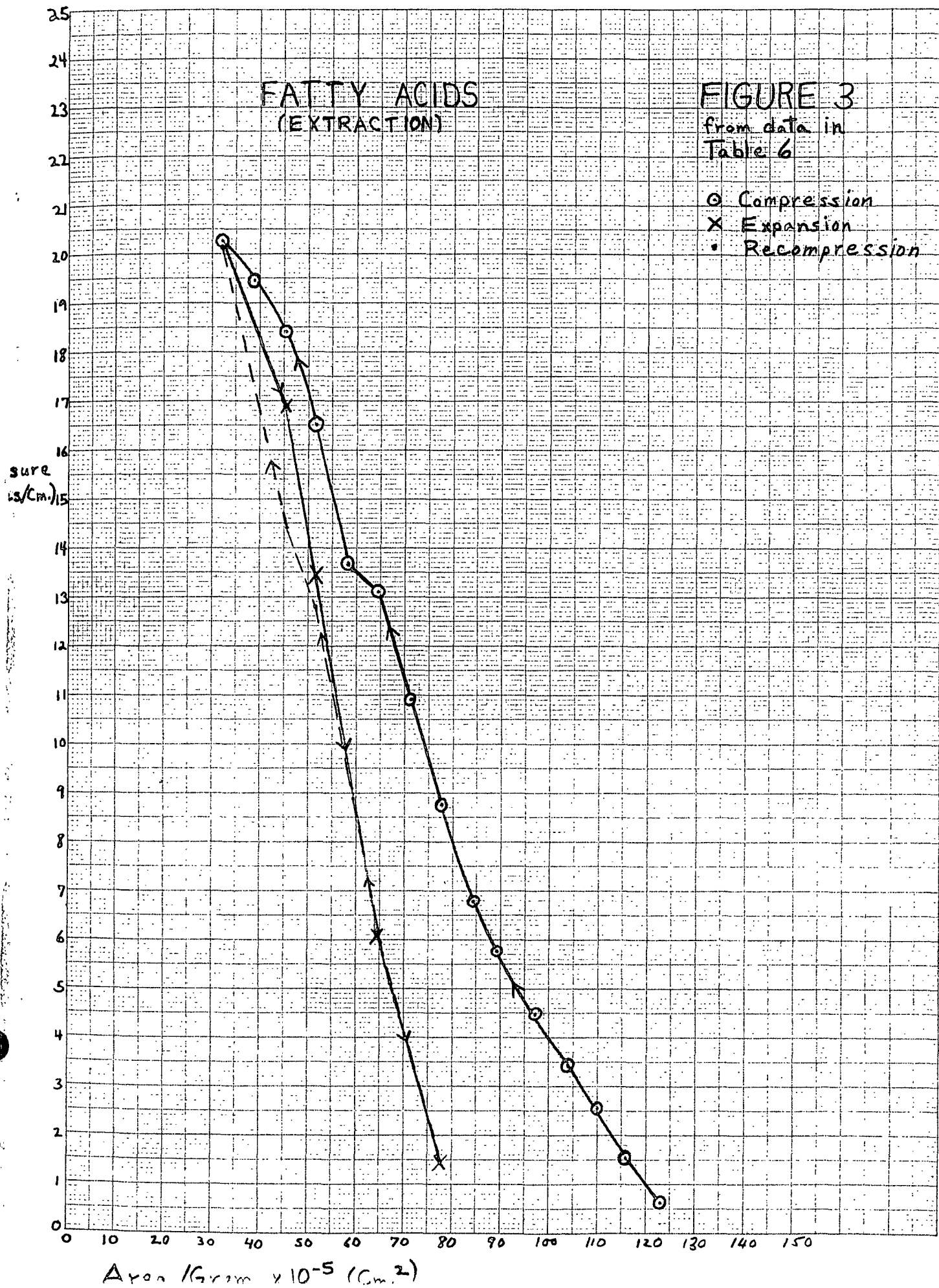
- Compression
- × Expansion
- Recompression

Pressure
#/cm.

Area / Gram $\times 10^{-5}$ (cm²)



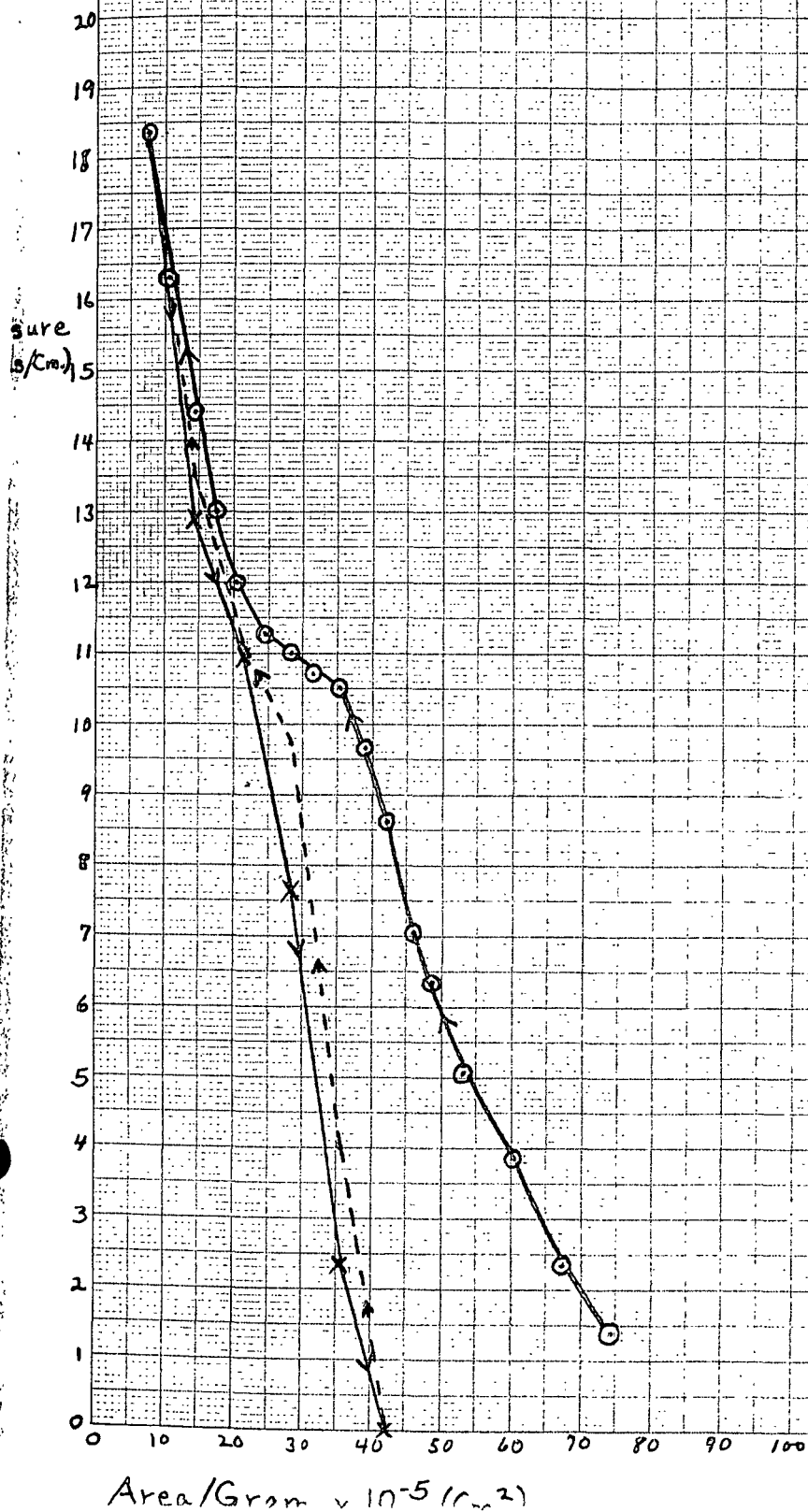




ROSIN ACIDS (FOAM)

FIGURE 4
from data in
Table 7

- Compression
- × Expansion
- Recompression



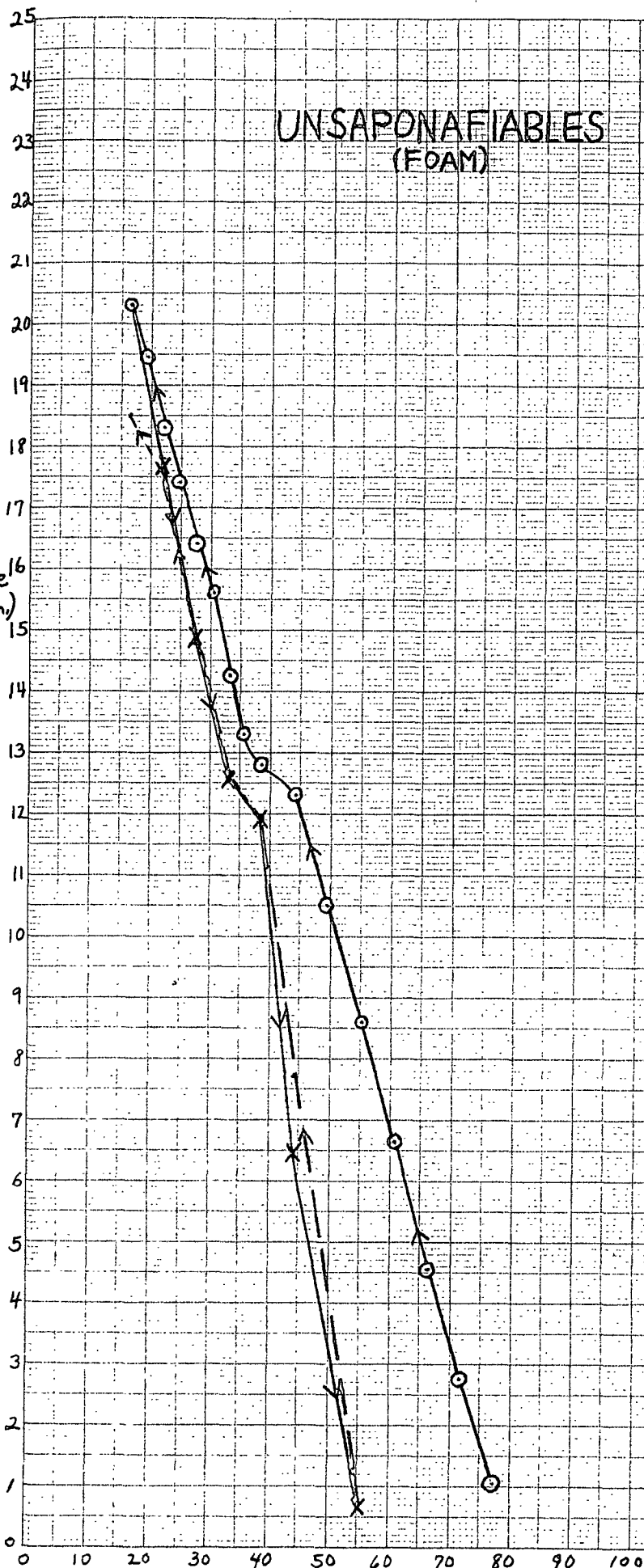
UNSAPOXAFIABLES (FOAM)

FIGURE 5

from data in
Table 10

- Compression
- x Expansion
- Recompression

Pressure
(g/cm²)



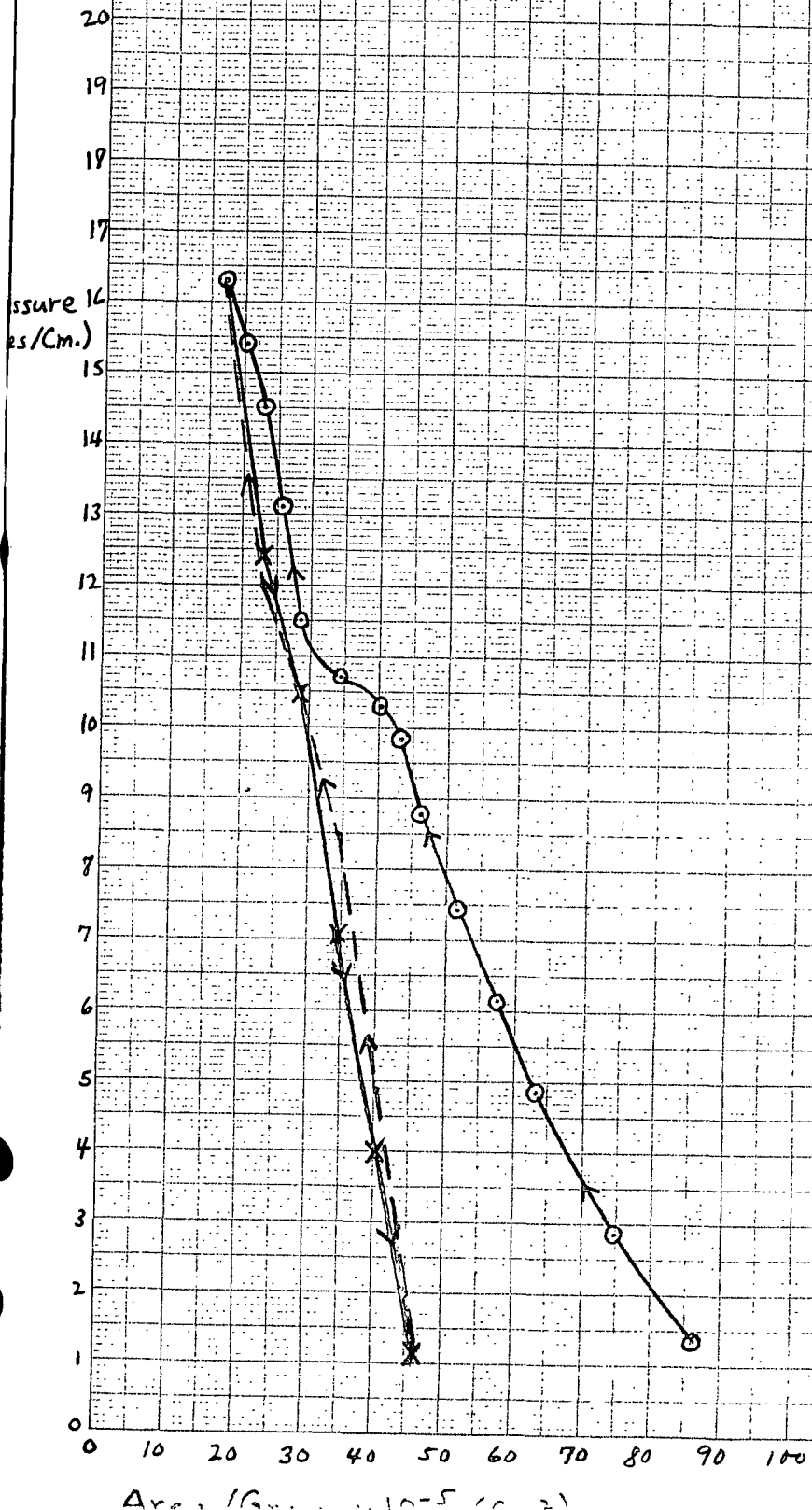
Area (cm²)

FATTY ACID ESTERS (FOAM)

FIGURE 6

From data in
Table II

- Compression
- x Expansion
- Recompression

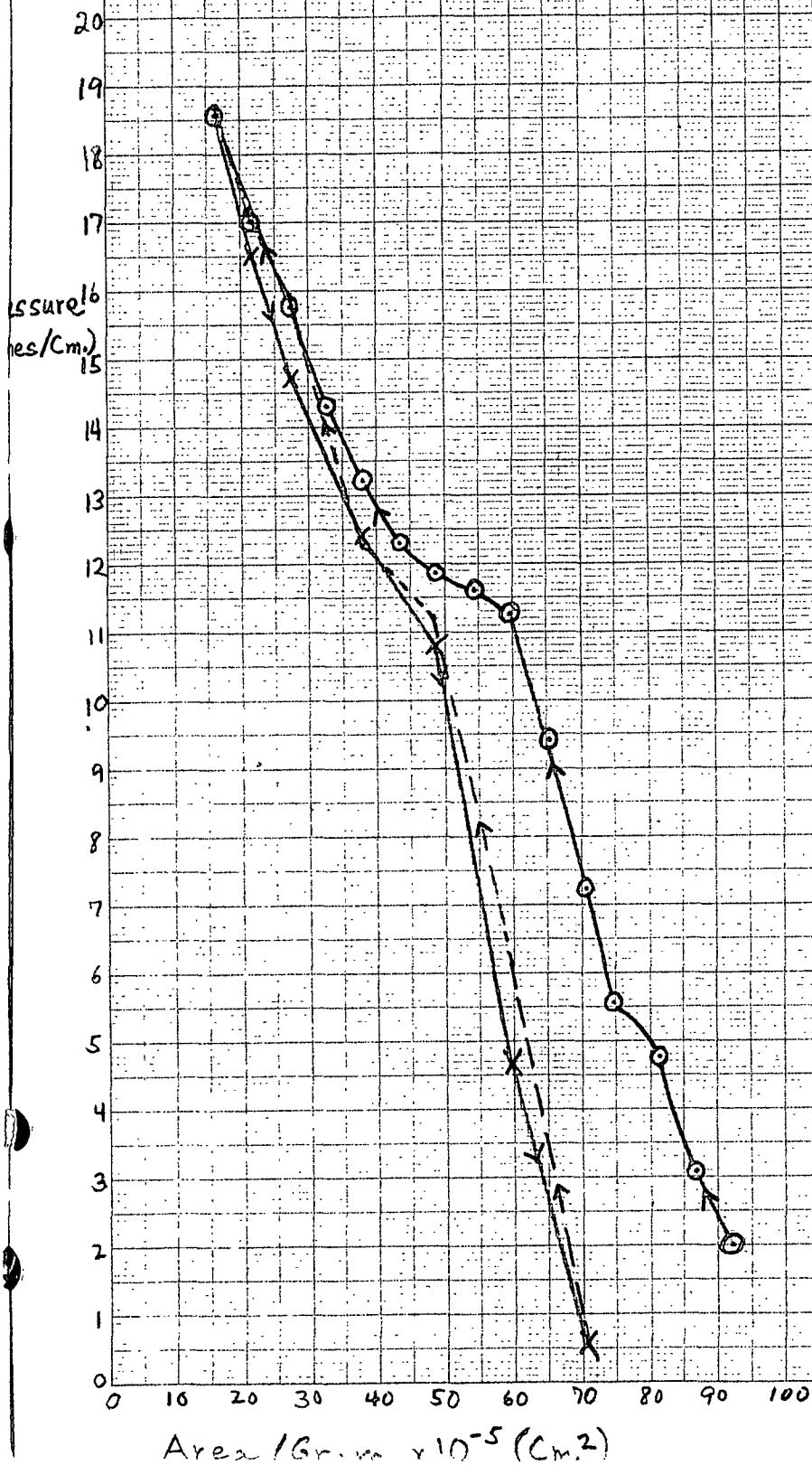


PITCH (EXTRACTION)

FIGURE 7

from data in
Table 13

○ Compression
x Expansion
· Recompression



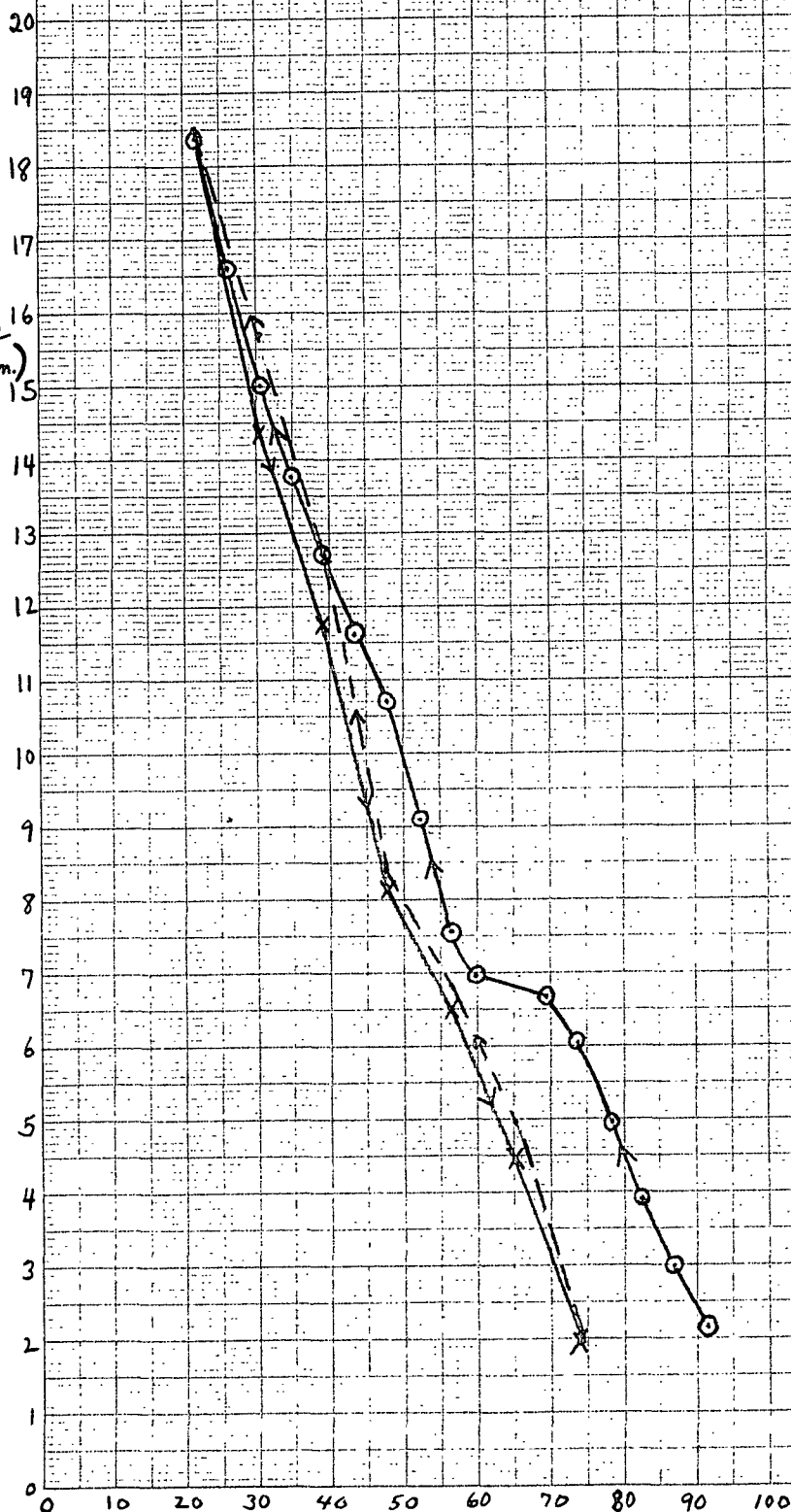
PITCH
(EXTRACTION)

FIGURE 8

from data in
Table 15

○ Compression
x Expansion
• Recompression

Pressure
(g/cm²)



Area (Gram x 10⁻⁵ cm²)

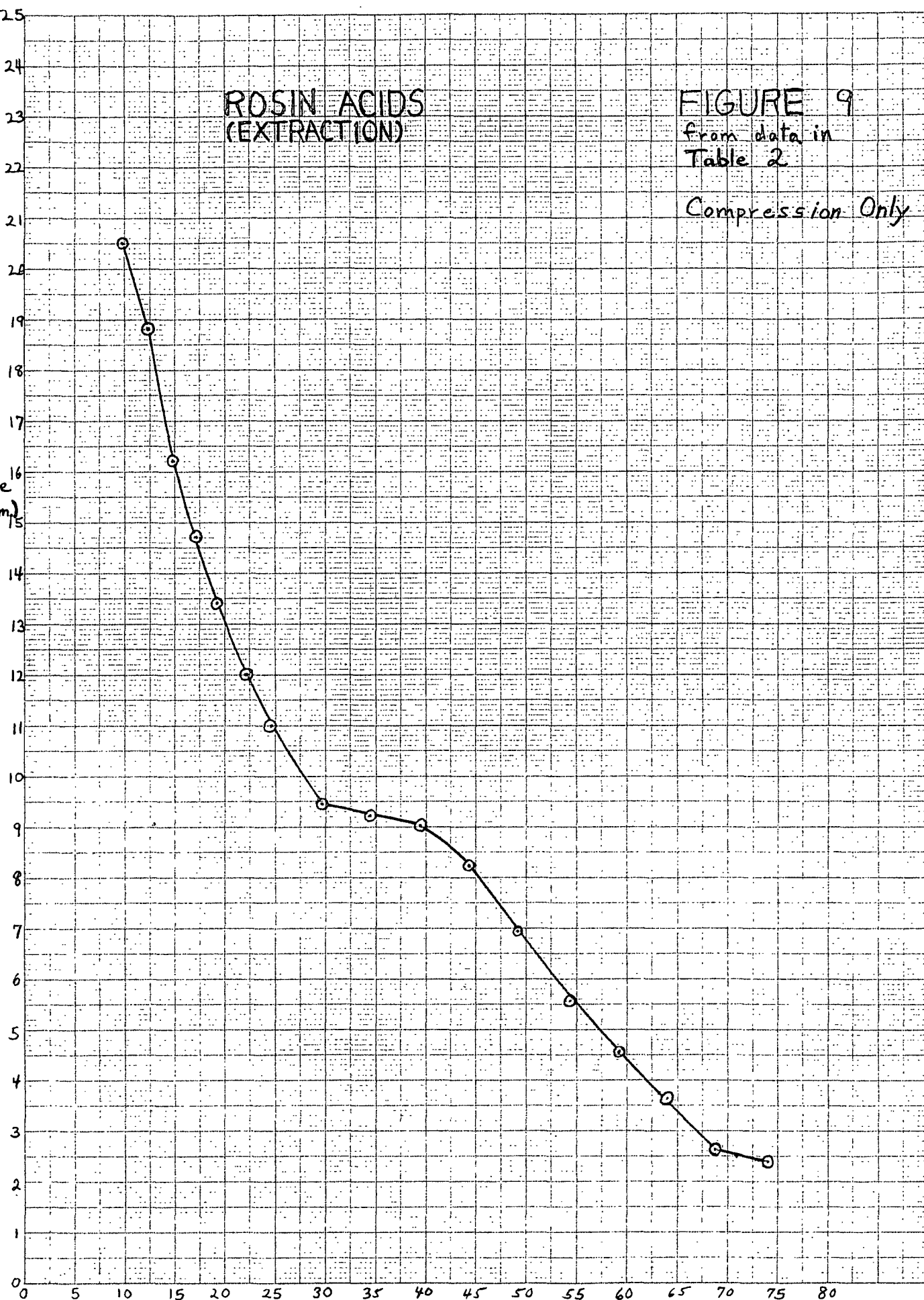
ROSIN ACIDS
(EXTRACTION)

FIGURE 9

from data in
Table 2

Compression Only

Pressure
(atm/cm)



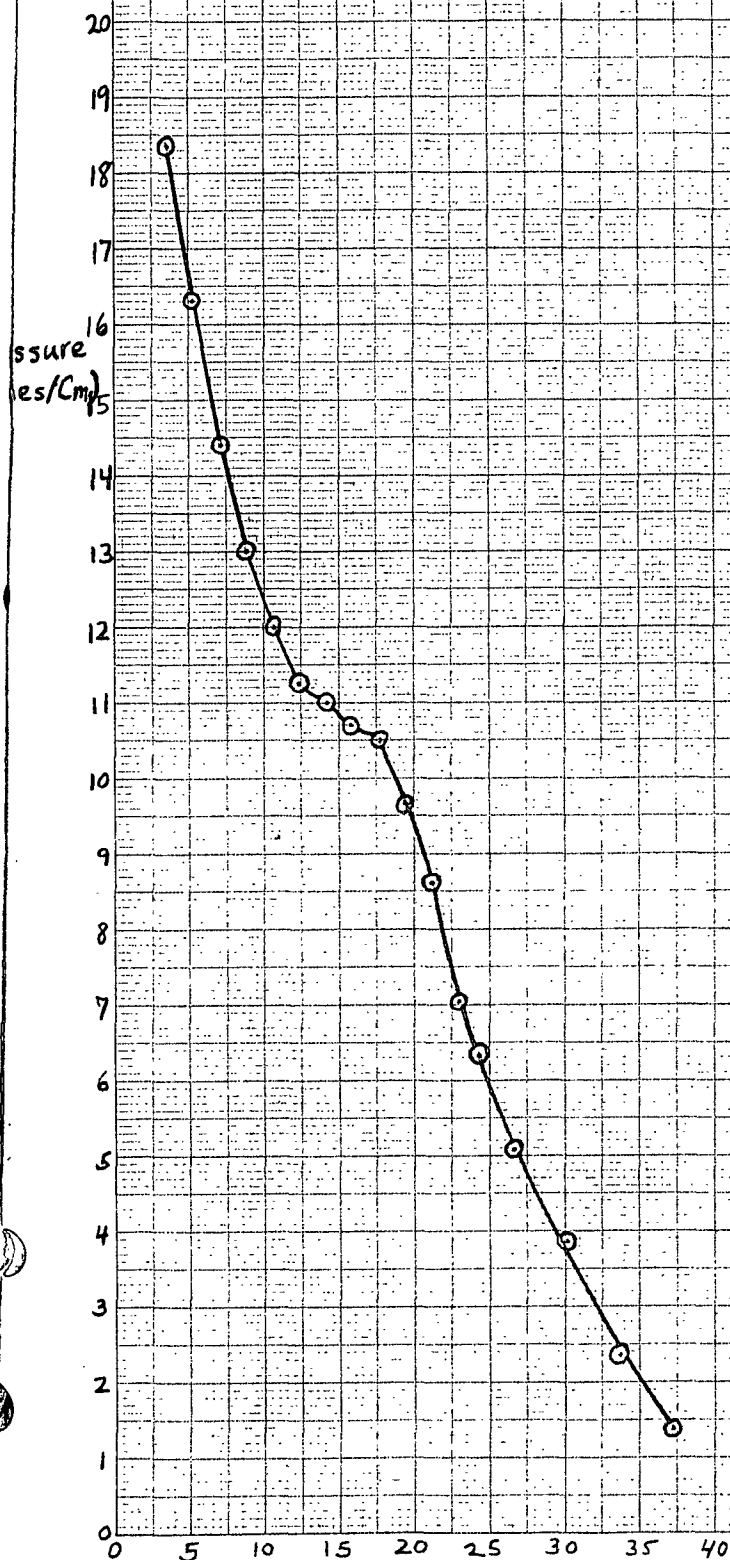
Area/Molecule (\AA^2)

ROSIN ACIDS
(FOAM)

FIGURE 10

from data in
Table 7

Compression Only



PROJECT REPORT FORM

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REPORT NO. 2 Chemistry
DATE March 12, 1956
NOTE BOOK 1248
PAGE 80 TO 140
SIGNED Shirley Mellen
Shirley Mellen

THE PITCH FILM OF SULFITE PULP

SUMMARY

This report is concerned with a number of aspects of the pitch problem: collections of pitch film from a calgon substrate, deposition of pitch film on a solid, chromatographic separation of pitch into its various constituents, and the conditions for the formation of a solid, rigid type pitch film.

Two methods of collecting pitch film were tried.

1. The collapse of a monomolecular layer of pitch film obtained by bubbling air through a hot water extract of sulfite pulp. A tap water substrate which contained 8×10^{-6} M calgon was used. The amount of pitch collected was not sufficient for analysis.

2. The collapse of a monomolecular layer of pitch film obtained by the dropwise addition of benzene-alcohol extract of sulfite pulp on the calgon tap water substrate. Analysis showed the pitch to contain 27.1% fatty acids, 9.3% resin acids, and 40.1% unsaponifiables.

Deposition of pitch film from alcohol-benzene extracts, hot and cold aqueous extracts, and hot alkaline extracts was investigated. The effect of pH, multivalent ions, and pressure were observed. Generally, the film deposited by "y" type deposition, but did not adhere to the solid

(a chromium-plated slide). The slide emerged wet from the solution, and on the immersion stroke, the deposited monomolecular film came off.

An exploration into the possibility of chromatographic separation of pitch film into various components showed no quick, easy application of the known procedures, which use Whatman No. 1 filter paper. Preliminary experiments with reversed phase paper chromatograms gave some indication of the usefulness of this type of chromatography once the technique is mastered. Column chromatography was not tried.

A series of qualitative film rigidity studies were done with hot aqueous and hot alkaline extracts. In order to obtain a solid rigid film, two conditions are necessary--a high pH (approx. 10) and the presence of calcium ion. A rigid film can be formed, at least temporarily, by bubbling nitrogen gas into a substrate of pH 8-9 with 10^{-3} M CaCl_2 . Unless calcium ion is present, pH appears to have little effect on film rigidity. Likewise, unless the pH is high, calcium ion has little effect.

INTRODUCTION

The deposition of pitch on various surfaces such as on the wire of a paper machine constitutes a major problem to papermakers. The basic hypothesis of this project is that pitch films form on the surface of water-pulp slurries. The folding and collapse of these films cause pitch ball formation and deposition of pitch on the paper machine. In an attempt to prove this hypothesis and to find a method of controlling or possibly alleviating pitch difficulties, a series of experiments were done on the surface film formed by a pitchy sulfite pulp. This report discusses several of these exploratory studies. In order to obtain conclusive evidence,

sections of this report should be repeated, and the work expanded.

EXPERIMENTAL RESULTS AND DISCUSSION

COLLECTION OF PITCH FILM

From information gained from preliminary experiments¹ using various substrates and modes of collection, it was decided to use an apparatus similar to that pictured in Figure 1 and a substrate of tap water 3×10^{-6} M in calgon* (using a molecular weight of 615).

A trough 4' x 1' x 1" was covered with fresh paraffin wax. Teflon tape was attached to the edges of the trough. The barriers were glass rods covered with teflon tape. No paraffin was put at the connection of the flask to the trough. The apparatus was the same as that shown in Figure 1 except a hole was not cut in the bottom of the flask. A gas dispersion tube was used to bubble air through the extract.

Sulfite pulp was obtained from the Flambeau Paper Company of Park Falls, Wisconsin. An approximate fiber analysis of a sample received January, 1956 showed the pulp to contain:

softwood sulfite (spruce, also some hemlock)	75%
hardwood sulfite (aspen and birch)	25%

Hot Water Extract

A 2-1/2 liter slurry of sulfite pulp containing approximately 1.3% pulp was heated to 95°C. with rapid stirring. It was stirred for fifteen minutes at this temperature and then filtered through a pad of filter-aid

*The crushed calgon was obtained from Calgon Inc., Pittsburgh, Pa.

APPARATUS FOR COLLECTION OF PITCH FILM

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March 12, 1956
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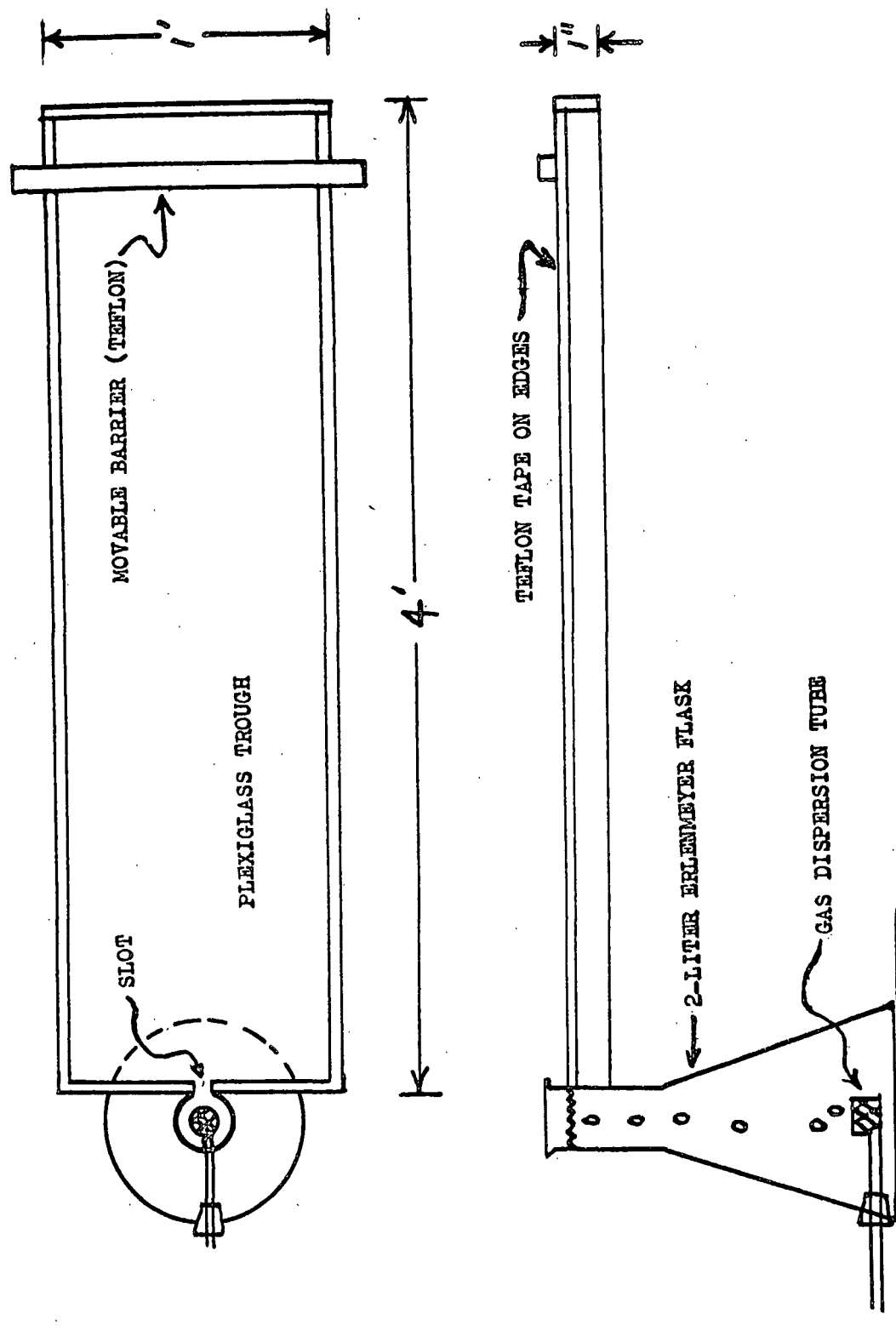


Figure 1

in a coarse porosity fritted glass funnel. The extract was cooled to about room temperature.

For about an hour, air was bubbled through the extract and a film was spread on the calgon substrate. The film was collapsed between two barriers and collected in an aluminum foil scoop. Fresh extract was added about every four hours (twice a day) and the substrate was changed every two days.

Gordon Hammes (1) found that there was fractionation in the film formation. The first films were of the gaseous type whereas later films became more rigid.

The amount of dirt and impurities from the air which settled on the film was discovered to be about 50% of the collection. A wooden and plastic cover was made to alleviate this situation. Only 11 mg. of dust-free pitch film was collected in a couple of weeks. This amount was not enough for an analysis.

Benzene-Alcohol Extract of Sulfite Pulp

Wet sulfite pulp was extracted in a soxhlet type apparatus for about six hours with benzene - 95% ethanol (2:1). The extract was concentrated on a hot plate under a stream of air.

The apparatus and substrate for the hot water extract films were used. The connection between the flask and the trough (labeled slot in Figure 1) was sealed off with paraffin wax.

The extract was placed dropwise on the calgon substrate. Fifteen minutes were allowed for benzene evaporation. The film was collapsed with the teflon-covered glass barriers and collected. Good film collapse was observed. The wet pitch film was scraped into a weighing bottle. It was partially dried by heating in a water bath under a stream of air and finally in a vacuum oven at 40°C. using concentrated H_2SO_4 as dehydrating agent. In this manner almost 100 mg. of pitch film was collected in a day. The substrate was changed twice a day. A total of 0.68 g. of pitch film was analyzed together with the benzene-alcohol extract. The results are given in Table I.

TABLE I
ANALYSIS OF PITCH FILM AND BENZENE-ALCOHOL EXTRACT

	Benzene 95% Ethanol (2:1) Extract of Sulfite Pulp	Film Collected From Benzene- Alcohol Extract
Fatty Acids, %	33.9	27.1
Resin Acids, %	9.7	9.3
Unsaponifiables, %	31.5	40.1
Total	75.1	76.5
Methoxyl, %	--	1.68

CHROMATOGRAPHY OF PITCH

Whatman No. 1 Filter Paper Chromatograms

Separation of the various components of pitch by paper chromatography was attempted but was not very successful. Whatman No.1 paper was spotted with pitch*, abietic acid, and tall oil. Chromatograms were run in the following solvent systems:

1. Butanol - pyridine - water (6:4:3 parts by volume)
2. Ethyl acetate - acetic acid - water (9:2:2)
3. Butanol - pyridine - water (10:3:3)
4. Butanol - acetic acid - water (63:10:27)
5. Iso-propanol - water (5:35)
6. The top layer of butanol - water - ammonium hydroxide (50:28:2)
7. Ethyl acetate - acetic acid - formic acid - water (15:3:1:4)
8. Butanol - ethanol - water (40:11:19)
9. Phenol - water (5:1), 3% of the water was formic acid
10. Propanol - ethanol - buffer (10:50:50)

the buffer was 1.6 N in respect to NH_3 and $(\text{NH}_4)_2 \text{CO}_3$

Areas were detected with ultraviolet light and with various sprays. The sprays which were tried are:

1. Bromothymol blue (2, 5). This spray is a very sensitive acid indicator. Either carbon dioxide from the air or acid remaining on the chromatogram from the use of an acid solvent system interferes with the detection of acid areas. Sometimes fogging the chromatogram with ammonia helped.

*The pitch sample was obtained from David Kortenberg

2. Starch spray (4). This acid indicator reagent is applied to chromatograms in two steps:

- a. 4% HCHO solution in ethanol is sprayed on the chromatogram.
- b. After drying, 0.5% KI and 0.2% KIO_3 dissolved in 2% starch solution is sprayed.

3. Phenol in CCl_4 (5). This is a good spray for resin acids but hazardous to handle. The chromatograms are sprayed with a 50% phenol solution, and then exposed to bromine vapors.

Table II gives the results of the observations of several of the chromatograms. Because the chromatograms did not show any separation and the detected areas were near the solvent front, it was decided to explore the possibilities of using reversed phase chromatography.

TABLE II

WHAARMAN NO. 1 FILTER PAPER CHROMATOGRAMS

Indicator	Solvent System			
	50 Butanol 28 Water 2 Ammonium hydroxide	10 Propanol 60 Ethanol 30 Buffer, 1.6 \underline{N} in respect to NH_3 and $(\text{NH}_4)_2\text{CO}_3$	3 Phenol 1 Water, 3% of which was formic acid	
Tall oil	Ultraviolet light	Blue fluorescence Rf 0.9	Smear near solvent front	Blue fluorescence
	Phenol spray (5)	Yellow, Rf 0.9	blue	purple-brown
	Color to the eye	--	--	yellow
Abietic Acid	Ultraviolet light	Smear near solvent front	Smear near solvent front	Some fluorescence
	Phenol spray	Smear near solvent front	blue	purple-brown
	Color to the eye	--	--	yellow
Pitch*	Ultraviolet light	Smear near solvent front	Smear near solvent front	Some fluorescence
	Phenol spray	--	blue	purple-brown
	Color to the eye	--	--	yellow

*The pitch area near solvent front was fluorescent under ultraviolet light, gave a slightly positive polorrhodol test, and a blue color with the iron reagent spray for phenolic substances.

Reversed Phase Chromatography

Whatman No. 1 filter paper was impregnated with various substances in an attempt to prepare a coated paper suitable for the chromatography of pitch. Those substances tried with the results obtained are listed below:

1. Dow Latex 512-K. Whatman paper was dipped in the latex, and was very heavily coated. The solvent front proceeded very slowly. Dilution of the latex with an organic solvent would be necessary in order to achieve a suitable paper for reversed phase work.

2. Quilon (6). Whatman filter paper was dipped in a 2% solution of Quilon. The paper was allowed to drip partially dry in the hood and then was dried in a 100-110°C. oven for about 5 to 10 minutes. The quilon-treated paper had a bluish cast to it, and water did not wet it.

3. "Mineral Spirits" (5). A 25% solution of "Mineral Spirits" in ether was prepared. Whatman paper was dipped in the ether solution, and the excess was removed by blotting.

4. Paraffin Oil. Whatman paper was dipped in paraffin oil and pressed dry between blotters. The paper appeared greasy. The solvent front was extremely slow and uneven. If paraffin oil is used again, it should be diluted, possibly with ether.

5. Armac H. T. Whatman paper was dipped in a 0.5% solution of Armac in water and pressed dry between blotters. The paper was heated in a 100-110°C. oven for 5 to 10 minutes.

A time study of the movement of the solvent front using the descending technique is given in Table III. Various solvent systems were tried. The term smearing indicates those chromatograms where the solvent front did not proceed evenly down the coated paper. Armac HI and paraffin oil would probably not give good chromatograms unless their coating media was diluted.

A group of reversed phase chromatograms were spotted with pitch, abietic acid, and tall oil. Table IV lists the areas which were detected with the phenol spray for resin acids.

Purified known samples of abietic-type resin acids* were chromatographed using the reversed phase technique. The phenol spray sensitive areas are shown in Table V. The unknown was the resin acid fraction of the surface collected pitch sample which was separated by the analytical department.

*Hercules Powder Company supplied the resin acids.

TABLE III

MOVEMENT OF SOLVENT FRONT ON REVERSED PHASE CHROMATOGRAMS

Solvent System	Treated Paper	Elapsed Time				1 hr.	3 hr.	4 hr.	5 hr.	6 hr.	12 hr.	24 hr.
		Start	25 min.	47 min.	52 min.	54 min.	44 min.	52 min.	29 min.	17 min.		
65 Iso-propanol	Quilon	0 cm.*	1.3 cm.	2.6 cm.	5.9 cm.	11 cm.	12.8 cm.	15.2 cm.	16.5 cm.	27.2 cm.	45 cm.	
35 Water	Armac HF	0	0	0	2	6.5	8.3	10.5	11.8	21.2	36	
	Mineral spirits	0	1.3	2.3	5	--	--	--	14.2	23.3	42	
	Paraffin oil	0	0	0	0	1.5	2**	3	3	7	15	
40 Butanol	Quilon	2	4.2	5.6	9.8	15.3	18	20.8	22.2	34	--	
11 Ethanol	Armac HF	0	0.5**	2	5	11.8	14	16.5	18	29.5	46.5	
19 Water	Mineral Spirits	1.7	3.5	4.8	8.6	17	--	18.8	20	30.5	46.5	
	Paraffin Oil	0	0	0	1	1	2**	2	2.5	4	15	
		Elapsed Time				1 hr.	3 hr.	4 hr.	5 hr.	6 hr.	12 hr.	24 hr.
		Start	27 min.	47 min.	52 min.	55 min.	47 min.	57 min.	31 min.	22 min.		
9 Ethyl Acetate	Quilon	3.2	6.3	8.5	10.5	22	25.5	29.8	31.2	49	--	
2 Acetic Acid	Armac HF	0	1.0**	2	4.8	8.2	10	17.8	19.5	34.2	--	
2 Water	Mineral Spirits	4.2	7.2	9.2	14.	24	27.3	32.2	34.8	52	--	
	Paraffin Oil	0	0	1	1	4.8	5.8**	7	7.5	16	38	
6 Butanol	Quilon	2.3	4.7	6.3	14	17	19	22.2	23.3	36.5	--	
4 Pyridine	Armac HF	0	0**	1.0	3.5	8	10	14	15	26	44	
3 Water	Mineral spirits	2.8	5	6.5	15	16.8	19	22	23.5	36	--	
	Paraffin oil	0	0	0	2	2	3.5**	2	2.5	5.5	15	
		Elapsed Time				1 hr.	3 hr.	4 hr.	5 hr.	6 hr.	12 hr.	24 hr.
		Start	25 min.	45 min.	57 min.	52 min.	42 min.	47 min.	27 min.	12 min.		
50 Butanol	Quilon	2	4.5	6	12	17	19.5	22	23	34	--	
28 Water	Armac HF	0	1.5	3	7	11.5	13	15.2	17	27	--	
2 NH ₄ OH	Mineral spirits	0.3	2.2	3.6	8	13	14.8	17	18	25	32	
(top layer)	Paraffin oil	0	0	0	0	0.5**	1	1.5	2	3.5	--	

* Centimeters solvent front moved from origin

** Smearing

TABLE IV

 REVERSED PHASE CHROMATOGRAMS SPRAYED WITH PHENOL SPRAY
 FOR RESIN ACIDS (5)

Whatman No. 1 paper treated with	Solvent System Used	Areas Reactive with Phenol Spray from			
		Abietic Acid	Tall Oil	Pitch	
Quilon	6 Butanol 4 Pyridine 5 Water	Color Rf* Yellow-brown 0.89	blue-pink 0.92	red-pink 0.86	
Quilon	40 Butanol 11 Ethanol 19 Water	Color Rf dark 0.85	dark 0.94	dark 0.91	
Quilon	65 Iso-propanol 35 Water	Color Rf yellow-green 0.91	yellow-green 0.93	-- --	
Quilon	50 Butanol 20 Water 2 NH ₄ OH (top layer)	Color Rf -- --	black 0.70	-- --	
"Mineral Spirits"	6 Butanol** 4 Pyridine 5 Water	Color Rf dark 0.78	dark 0.97	dark 0.97	
"Mineral Spirits"	40 Butanol 11 Ethanol 19 Water	Color Rf dark 0.85	dark 0.89	dark 0.89	
"Mineral Spirits"	65 Iso-propanol*** 35 Water	Color Rf black 0.95	black 0.93	black 0.93	
"Mineral Spirits"	50 Butanol 20 Water 2 NH ₄ OH (top layer)	Color Rf streaked 0.25	streaked (poor chromatogram)	0.91	
Armac JET	65 Iso-propanol 35 Water	Color Rf dark 0.89	dark 0.89	red and dark 0.00 0.89	

*The ratio of the distance the spot traveled from the origin to the distance the solvent front moved.

**Areas at Rf 0.91 reacted with the acid indicator spray bromothymol blue.

***These same areas were visible under ultraviolet light.

TABLE V

CHROMATOGRAMS OF RESIN ACIDS

	Ultraviolet Light	Phenol Spray for Resin Acids (5)
Isobutyric acid	no fluorescent areas	green streak
Dehydroabietic acid	no fluorescent areas	no reaction
Mixed dihydroabietic acid and tetrahydroabietic acid	no fluorescent areas	violet streak
Unknown Resin acid fraction of pitch	Blue streak (Rf 0.5) blue fluorescent areas (Rf. 0.6 and 0.85)	no reaction
Solvent system 65 Iso-propanol 35 Water Whatman paper treated with quilon		

CONDITIONS FOR PITCH DEPOSITION

A series of experiments were conducted to determine under what conditions a pitch film deposits on a solid, and does or does not adhere to that solid. The first experiments were performed using a paraffin-coated pyrex trough 9"x15"x2" (Figure 2), and manually controlling the movement of the slide. After a few preliminary attempts, it was decided to use a deeper trough and a dipping apparatus (Figure 3).

A chromium-plated slide was used as the solid. The slide was thoroughly soaped with alkanox and rinsed in tap water. It was then scoured with wet celite filter-aid. The final rinsing was done in tap water holding the slide with a pair of tweezers. A monomolecular layer was deposited on the slide by the following methods:

1. Stearic acid. The slide was dipped repeatedly in a benzene solution of stearic acid with drying intervals. It was polished with diaper cloth to leave only a monomolecular layer of stearic acid.
2. Pitch. The clean, wet slide was placed in the trough at point C (see Figure 3). The benzene-alcohol extract was added. After time was allowed for benzene evaporation, the slide was withdrawn and air dried.
3. Wet. Occasionally, the clean, wet slide was used with no monomolecular layer deposited on it. The benzene-alcohol extract was first placed on the substrate. Time was allowed for benzene evaporation. The slide was then dipped into the pitch film.

APPARATUS FOR PITCH DEPOSITION



Figure 2

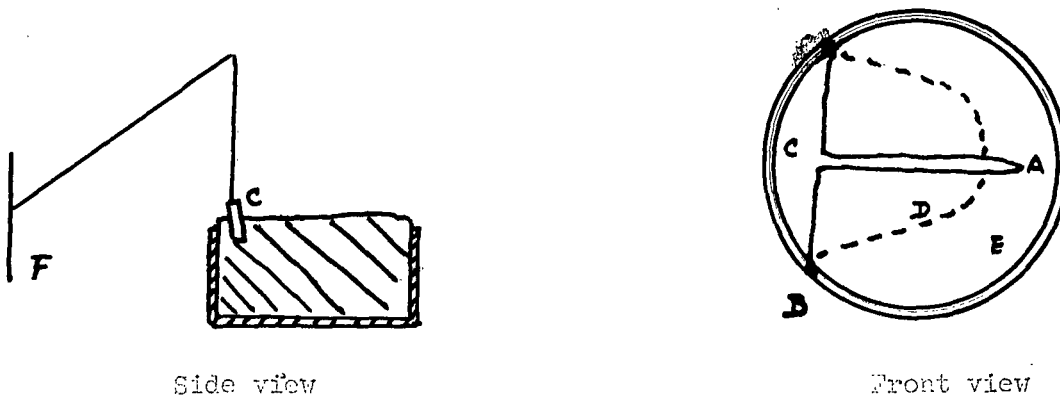


Figure 3

- A. Teflon thread
- B. Attachment for teflon thread
- C. Point for pitch addition and slide dipping
- D. Teflon thread expanded after addition of pitch
- E. Position for piston oil addition
- F. Dipping apparatus

Deposition experiments were done (1) by spreading a film from the benzene-alcohol extract of sulfite^{pulp} on a substrate and (2) with hot and cold aqueous and hot alkaline extracts of sulfite pulp.

Table VII, in the appendix, gives the conditions and the results of the experiments performed with the benzene-alcohol extract. The substrate was poured into the freshly paraffin-coated pan of Figure 3. Several drops of benzene-alcohol extract were added at C. Fifteen minutes were allowed for benzene evaporation. Pitch film deposition on the chromium-plated slide was observed with substrates of tap water and distilled water at different pH's, with Blodgett's substrate for best stearic acid deposition (7) and with two alum substrates (8). Two piston oils were tried, oleic acid and castor oil ($\gamma = 29.5$ dynes/cm. and $\gamma = 16$ dynes/cm., respectively). It was extremely difficult to observe the movement in (toward C) or out of the teflon thread with castor oil as piston oil.

Under most conditions the film deposited by γ type deposition for a single cycle (one immersion and one emersion). There was no deposition when the slide was moved in and out of the substrate rapidly.

A group of deposition experiments using aqueous and alkaline extracts of the sulfite pulp was performed. Tables VIII and IX of the appendix give information about these experiments. The results were the same as those observed for the pitch film of the benzene-alcohol extract. The apparatus shown in Figure 3 was used. The extract was poured into the paraffin-coated pan. Time was allowed for film formation. The surface was swept halfway with a barrier and a teflon thread was attached. It was found necessary to add piston oil in order to more easily observe movement of the teflon thread.

At a high alkaline pH and with 10^{-2} M CaCl_2 , brown and white crystals deposited on the slide. The crystals were analyzed to be of the appendix CaCO_3 . Table X shows the conditions for CaCO_3 formation.

Attempts were made to measure the thickness of the pitch film. Sulfite pulp extract was acidified and H_2 gas was passed into the solution. The extract was made alkaline and 10^{-5} M CaCl_2 was added. Film went on the stearic acid step wedge (9) by x type deposition. Comparison with another step wedge showed the pitch to have shifted it about 2 wedges. Therefore one layer of pitch is equivalent to two layers of stearic acid or about 50 Å.

QUALITATIVE FILM RIGIDITY STUDIES

A study of the film formation on hot water and hot alkaline extracts of sulfite pulp was undertaken to investigate the relationship between conditions, length of time, and the type of film formed.

Because of the qualitative nature of this series of experiments, very general terms of classification of the film formed were used. (Harkins (10) gives a much more elaborate system, but precise instruments are needed.) A piece of bond paper is cut (about 0.5 x 3 cm.) and folded in thirds to form a boat. It is placed on the surface of the film and blown. The extent of the boat's movement qualitatively measures the film rigidity. The following terms with their respective meaning indicated the state of the pitch film:

1. Gaseous. When blown on, the boat moved freely and in no particular direction. Movement continued after blowing ceased.

2. Gaseous - liquid. The boat moved freely in the direction blown. Movement continued after blowing ceased.

3. Liquid. The boat moved in the direction blown and stopped when the blowing ceased.

4. Liquid - solid. The boat showed some resistance to moving in the direction blown.

5. Solid. When blown on, the boat resists movement. It practically snaps back into its original position. This indicates a rigid film.

A hot-water extract and a hot-alkaline extract of sulfite pulp were acidified with hydrochloric acid and nitrogen gas was bubbled into the extract through a gas dispersion tube. The extract was poured into a paraffin-coated petri dish and film formation was observed in a dust-free enclosure.

Elapsed of time and film rigidity were recorded for different pH's and some with 10^{-3} M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. The results are shown in Table VI. One experiment was done at a high pH with calcium ion present to observe the effect of calgon addition. This film was extremely rigid.

General conclusions which can be drawn from the film formation studies are:

1. A high pH and the presence of calcium ion produce a rigid film.
2. The removal of dissolved CO_2 from the water by bubbling H_2 gas into the extract may aid, at least temporarily, in the formation of a rigid film.
3. The presence of calgon in the extract aids in the formation of a rigid film.
4. Film formation is rapid and its final state is reached in a few minutes.

FUTURE WORK

Collection of the pitch film formed from the hot alkaline extract of sulfite pulp might prove of interest. The extract could be acidified and nitrogen gas bubbled in to expel air before a film is spread from the extract.

Further work using chromatographic means of separation of pitch components should yield a good method for determining pitch constituents. More use of the reversed phase technique is needed to develop it into a usable instrument for chromatographic work. Column chromatography using Magnesol or another adsorbent may prove valuable.

Future pitch deposition studies should be done with more elaborate apparatus. A long shallow rectangular trough with a deep well at one end is needed. The material used to make the apparatus should be paraffin-covered plexiglass. It might be advantageous to place a stopcock in the bottom in order to facilitate quick and easy removal of the substrate. A film pressure sensitive device might also be included.

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The role of solubilization should be studied in an attempt to understand the importance of this phenomenon to the pitch problem. The ether solubles of a hot alkaline and an alum extract of the pitchy sulfite pulp could be determined.

TABLE VI
FILM RIGIDITY STUDIES

Conditions	Elapsed Time,		Rigidity of Film (Boat Test)
	hours	minutes	
<u>Hot Water Extract of Sulfite Pulp</u> The effect of pH pH 3.4 (HCl added)		0	gaseous
		20	gaseous
		30	gaseous
		50	gaseous
	1	5	gaseous
	1	25	gaseous-liquid
	1	45	gaseous-liquid
	2	0	gaseous-liquid
	4	15	gaseous-liquid
	4	30	gaseous-liquid
	23		gaseous-liquid
		0	gaseous
		35	gaseous-liquid
pH 6.3		50	gaseous-liquid
	1	10	gaseous-liquid
	1	20	gaseous-liquid
	1	45	gaseous-liquid
	4		gaseous-liquid
	4	15	gaseous-liquid
	23		gaseous-liquid
		0	gaseous-liquid
		20	gaseous-liquid
		35	gaseous-liquid
pH 10.5 (NaOH added)		55	gaseous-liquid
	1	15	gaseous-liquid
	1	30	gaseous-liquid
	3	45	gaseous-liquid
	4		gaseous-liquid
	4	30	gaseous-liquid
	22	30	gaseous-liquid
		0	gaseous-liquid
		15	gaseous-liquid
		45	gaseous-liquid
The effect on Ca ion (10^{-3} M CaCl_2) pH 7.1	19		gaseous-liquid
		0	gaseous-liquid
		15	gaseous-liquid
		45	gaseous-liquid
pH 10.5		0	gaseous-liquid
		15	solid
		40	solid
	17		liquid-solid

TABLE VI (Continued)

Conditions	Elapsed Time, hours minutes		Rigidity of Film (Boat Test)
<u>Hot Alkaline Extract of Sulfite Pulp</u>			
The effect on pH			
pH 2.5		0	gaseous
		15	gaseous
		35	gaseous-liquid
	1		gaseous-liquid
	4		gaseous-liquid
pH 6.9	5		gaseous-liquid
		0	gaseous
		25	gaseous-liquid
		50	gaseous-liquid
	3	50	gaseous-liquid
4	5	gaseous-liquid	
4	45	gaseous-liquid	
pH 10		0	gaseous
		15	gaseous-liquid
		40	gaseous-liquid
	3	40	gaseous-liquid
	4		gaseous-liquid
4	35	gaseous-liquid	
The effect of Ca ion (10^{-5} M CaCl_2)			
pH 6.3		0	gaseous-liquid
		15	gaseous-liquid
		55	gaseous-liquid
pH 8.5		0	gaseous-liquid
		20	gaseous-liquid
		35	gaseous-liquid
		45	gaseous-liquid
Bubbled H_2 into the solution			about a liquid
Stood approx. 30 min.			gaseous-liquid
pH 9.2		0	gaseous-liquid
		10	gaseous-liquid
		25	gaseous-liquid
		40	gaseous-liquid
Bubbled H_2 into the solution			solid
Stood approx. 30 min.			liquid
pH 10.5		0	gaseous-liquid
		15	liquid-solid
		50	solid

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APPENDIX

TABLE VII

CONDITIONS FOR PITCH DEPOSITION ON SOLIDS
BENZENE ALCOHOL EXTRACT OF SULFITE PULP

Substrate	pH	Temp. °C.	Piston Oil	State of Pitch Film (Boat Test*)	What is deposited as monomolecular on chromium-plated slides	Type Deposition	Remarks
Blodgett K ₂ CO ₃ BaCl ₂ CuCl ₂	10.5 (NaOH added)	Room Temp.	Oleic Acid		Stearic Acid	y	Teflon thread moved in on both immersion and emersion strokes
Blodgett K ₂ CO ₃ BaCl ₂ CuCl ₂	11.5 (NaOH added)	Room Temp.	Oleic Acid		Stearic Acid		When oleic acid was added, the pitch film was greatly com- pressed as evidenced by a sharp movement in of the teflon thread. Could not control the slide well enough to keep from wetting the edges.
Tap water	10.0	18	Oleic Acid		Stearic Acid	y	Very slow deposition (10 min. cycle). Difficult to observe, but thread appears to move in on both strokes.
Tap water	10.0	17	Oleic Acid		Stearic Acid	None	Rapid strokes emersion--film on; wet slide immersion--film off
Tap water	9.6	16	Oleic Acid		Pitch Wet slide Stearic acid	y y y	Slow single cycle for each slide.
Tap water	9.5	10	Oleic Acid		Stearic acid	y	One slow cycle
Tap water	9.2	25	Oleic Acid		Pitch	y	Very slow deposition (10-15 min./cycle)

*An explanation of the boat test is given on page 18 of this report.

TABLE VII (Continued)

water	9.2	25	Oleic Acid	gaseous	Pitch	y	One single, slow cycle
					wet slide	y	
					stearic acid	y	
water	8	17	Oleic Acid		Pitch	y	One slow cycle
					stearic acid	y	
water	6.0	26	Oleic Acid		Pitch	y	One slow cycle
					wet slide	y	
					stearic acid	y	
water	6.2	15	Oleic Acid	gaseous	Pitch	y	One slow cycle
					wet slide	y	
					stearic acid	y	
water	5.8	13	Oleic Acid	gaseous	Pitch	y	One slow cycle
					wet slide	y	
					stearic acid	y	
water	5.7	21	Oleic Acid	gaseous	Pitch	y	One slow cycle
					wet slide	y	
					stearic acid	y	
water	3.6	12	Oleic Acid		Pitch		Could not keep from wetting slide.
water	2.0	Room Temp.	Oleic Acid		Pitch	y	One slow cycle
					Wet	None	(Up stroke--thread in
					stearic acid	None	(Down stroke--thread out
water	2.0	Room Temp.	Oleic Acid		Stearic Acid	x, y	Slow deposition (20-25 min./ cycle) down stroke--thread in difficult to tell on upstroke
water	9.1	18	Castor Oil	gaseous	Pitch	y	Slow cycle
					wet slide		upstroke--thread in difficult to tell on downstroke
water	8.0	17	Castor Oil		Pitch	y or x	Difficult to tell movement of thread on upstroke
					stearic acid	x, y or none	Slow cycle

TABLE VII (Continued)

Tap water	7.2	Room Temp.	Castor oil		Pitch	None	No apparent movement of thread for 6 cycles
					stearic acid	None	downstroke--thread in upstroke--thread out
Tap water	6.0	26	castor oil	gaseous	Pitch	x, y	Slow cycles, very difficult to observe movement of thread especially on upstroke.
					wet stearic acid	y	Appears to move in
Tap water	6.5	Room Temp.	castor oil		Pitch	none	One slow cycle
Tap water	5.0	24	castor oil		Stearic acid	none	Slow 10-min. cycle
						none	Rapid cycles down--thread out up--thread in
Tap water	2.6	Room Temp.	castor oil		Pitch	none	after about 12 cycles some deposition when slide is moved up rapidly.
Dist. water	6.5	24	oleic acid gaseous state	gaseous- liquid	Pitch	none	one rapid cycle; 1 slow c. (3 min.) z-type, wet slide, then off.
Dist. water	4.7 (H ₂ SO ₄ added)	25	oleic acid gaseous	gaseous	Pitch	y none	one slow cycle z-type, wet slide, film moves off
Dist. water	6.4	25	oleic acid gaseous	gaseous- liquid	Pitch) wet) stearic)	y none	one slow cycle z-type, wet slide, film moves off (10-sec. cycles)
Alum solution A	5.9- 4.0	23	oleic acid	gaseous	pitch	y)	one slow cycle
					wet	y)	
					stearic acid	y)	
		24			pitch, wet	none	
		21			stearic acid		z-type, wet slide, film moves off (20-sec. cycles)

TABLE VII (Continued)

Alum solution A	4.2 (NaOH added)	24	Oleic acid gaseous-liq.	liquid	Pitch	y none	One slow cycle z-type, wet slide, off (if allow slide to dry, film will again deposit on downstroke.--y type deposition.)
Alum solution B	5.0	21	Oleic acid	gaseous	Pitch wet stearic acid	y	One slow cycle
	5.3	24	Oleic acid	gaseous	Pitch stearic acid	none	
	6.1- 6.2	25	Oleic acid	liquid	Pitch wet stearic acid	none	z-type, wet slide, film off (if allow slide to dry, film will again deposit on downstroke.-- y type deposition.)

TABLE VIII

CONDITIONS FOR PITCH DEPOSITION ON SOLIDS
HOT WATER EXTRACT OF SULFITE PULP

Exp. No.	pH	Temp. °C.	Rigidity of Pitch Film (boat test)	No Piston Oil 1 Cycle	Repeated Cycles	Piston Oil 1 Cycle	Repeated Cycles	Remarks
1	5.5-5.6	25	gaseous	--	none	--	--	x-type deposition, then film moved off.
	2-4	25		y	x	--	--	H ₂ SO ₄ injected into substrate
	8-10	25	--	y	none	--	--	x-type deposition for 10 sec. cycles.
	3-10	25	--	y	none	--	--	for rapid repeated cycles. NaOH injected into substrate
2								10 ⁻² M CaCl ₂ injected into substrate.
	5.3	24	--	--	--	--	none	
	4	24	--	--	--	x	none	H ₂ SO ₄ injected into substrate
3								deposition on 10 sec. strokes.
	10	24	--	--	--	x	none	NaOH injected into substrate.
3	5.3	24	gaseous	?	?	--	--	No observed movement of teflon thread
	5.3	24	gaseous	--	--	x	some	Some deposition on emersion and immersion stroke on areas of the slide which were dry.
4								
	2	24	--	--	--	x	none	H ₂ SO ₄ added
5								
	2.3	24	--	x	some	--	--	Some deposition on emersion and immersion stroke on areas of the slide which were dry.
5								
	2.3	24	--	--	--	x	some	Some deposition on emersion and immersion stroke on areas of the slide which were dry.
6								
	11.3	24	--	--	--	x or y	--	Difficult to observe movement of teflon thread.
7								
	5.8	24	gaseous	?	?	--	--	Difficult to observe movement of teflon thread.
	5.8	24	gaseous	--	--	y	none	Film deposits on emersion stroke and spreads back on the substrate on immersion.

TABLE VIII (Continued)

7	5.8	24	gaseous	--	--	y	none	10^{-2} M CaCl_2 added. Film deposits on emersion stroke and spreads back on the substrate on immersion.
8	5.6	25	liquid	?	?	--	--	Difficult to observe movement of teflon thread.
	5.6	25	liquid	--	--	y	none	Film deposits on emersion stroke but spreads on substrate on immersion.
	5.6	25	liquid	--	--	y	none	10^{-2} M CaCl_2 added. Film deposits on emersion stroke but spreads on substrate on immersion.
9	6.5	22	gaseous	?	?	--	--	Difficult to observe movement of teflon thread.
	6.5	22	gaseous	--	--	y	none	Film deposits on emersion stroke, but spreads on substrate on immersion.
	6.5	22	--	--	--	y	none	10^{-2} M CaCl_2 added. Film deposits on emersion stroke, but spreads on substrate on immersion.
10	2.7-2.8	25	solid	?	?	--	--	Difficult to observe movement of teflon thread.
	2.7-2.8	25	solid	--	--	y	none	Film deposits on emersion stroke, but spreads on substrate on immersion.
11	11.3	25	solid	--	--	y	none	10^{-2} M CaCl_2 added very blotchy film deposited on slide.

TABLE IX

PITCH DEPOSITION STUDIES

FILM FORMED ON HOT WATER EXTRACT OF BLEACHED SULFITE PULP

Experiment No.	pH	Temp., °C.	Film Rigidity Boat Test* Pitch Film	Type of Deposition				Remarks
				No Piston Oil One Cycle	Repeated Cycles	Piston Oil One Cycle	Repeated Cycles	
1	9-10 (NaOH added)	23	--	y (?)**	none	--	--	--
	9-10	23	--	--	--	y	none***	--
2	8.1	22	Liquid-solid	***	***	--	--	--
	8.1	22	Liquid-solid	--	--	y	none***	--
	8.1	22	Partially solid	--	--	y	none***	10 ⁻² M CaCl ₂ injected into substrate
3	5.7	23	Liquid-solid	***	--	--	--	--
	5.7	23	Liquid-solid	--	--	y	none***	--
	5.7	23	--	--	--	y	--	10 ⁻² M CaCl ₂ injected into substrate
4	4	23	gaseous	***	--	--	--	--
	4	23	--	--	--	y	none***	--
	4	23	--	--	--	y	none***	10 ⁻² M CaCl ₂ injected into substrate

*Boat test explained on page 18

**Difficult to observe any movement of teflon thread

***Film deposits on emersion. The slide is wet and the film spreads on substrate on immersion.

TABLE X

CONDITIONS FOR DEPOSITION OF CaCO_3

Substrate	pH	Temp., °C.	Conc. of CaCl_2	Deposition of CaCO_3 and Pitch	Type Deposition one Cycle	Remarks
1. Cold water slurry of sulfite pulp	--	--	No CaCl_2 added	--	x	Film deposited on immersion stroke
2. Filtrate of cold water slurry of sulfite pulp	--	--	No CaCl_2 added	--	x	Film deposited on immersion stroke
3. Cold water slurry of sulfite pulp	alkaline	--	10^{-2} <u>M</u>	yes	y	White crystals visible under microscope
	11.2	24	10^{-4} <u>M</u>	yes	?	Some white crystals. Difficult to tell type deposition. Film in solid state
	9.3	24	No CaCl_2 added	yes	y	Maybe some white crystals. Film in solid state
	11.5	--	10^{-3} <u>M</u>	yes	y	Some white crystals
	11.3	25	10^{-2} <u>M</u>	yes	y	White crystals
4. Hot water extract of sulfite pulp	11.5	22	10^{-4} <u>M</u>	yes	y	White crystals

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SURFACE CHEMICAL STUDIES ON PITCH FILMS

SUMMARY

This report is a continuation of work begun and described in Project Reports 1 and 2. (1, 2). It is divided into four sections; solubilization of pitch, surface viscosity of pitch film, collection of pitch film, and surface balance studies of pitch and its components.

In an attempt to understand what roll solubilization might play in the pitch problem, hot alum, hot alkaline, and hot water extracts of a sulfite pulp were prepared. The amount of ether soluble materials in the three extracts was 0.05-0.10% of the pulp. These results did not show any significant differences in the amount of pitchy substances removed.

The surface viscosity of pitch film spread on calgon and/or alum substrates at different pH's was observed. The presence of aluminum ion gave a solid, rigid film at a neutral or a slightly acid pH, depending on the concentration of alum. The addition of calgon did not appreciably effect the surface viscosity.

Table V gives an analysis of pitch films collected by:

1. Collapse of monolayers of pitch film obtained by bubbling air through a hot alkaline extract of Flambeau sulfite pulp. A distilled water substrate containing 10^{-4} M aluminum ion was used.

2. Collapse of monolayers of pitch film obtained by bubbling air through hot alkaline, hot water, and hot acid extracts of sulfite pulp. This study showed that at lower pH's less film was collected and the film formed on the substrate was less rigid. The table also gives an analysis of a benzene-alcohol extract. A known sample of stearic acid, abietic acid, and unsaponifiables was prepared and analysed. A 95% recovery was made.

Pressure-area curves, (Figures 1-21), were obtained for pitch and its fractions by means of a surface balance. The substrates used were dilute hydrochloric acid, distilled water, * sodium hydroxide, distilled water containing 3×10^{-4} M aluminum ion, and tap water containing 8×10^{-6} M Calgon. Table VI summarizes the properties of the films illustrated in the figures.

EXPERIMENTAL RESULTS AND DISCUSSION

Solubilization of Pitch

Hot alum (0.5% alum solution), hot alkaline (pH 10), and hot water (pH 5-7) extracts of Flambeau sulfite pulp were prepared using a 2 1/2-3 liter slurry. The pulp slurries were heated to 95°C. with constant, rapid stirring and were filtered while hot. After cooling, the filtrates were neutralized to approximately pH 7 and concentrated either at reduced pressure or on a hot plate under a stream of air.

* The water used in these experiments was distilled twice, unless otherwise indicated.

The concentrates were then extracted three times with ether. The amount of ether soluble materials was determined on the basis of oven-dry pulp. Table I shows that there was little difference in the amount of ether solubles in the three pulp extracts. The large range shown for the hot alkaline extract may be due to the difficulty encountered in making a clean separation of the ether-water layers.

TABLE I

Extract	Ether soluble material
Hot alkaline	0.05-0.10%
Hot alum	0.06-0.07%
Hot water	0.05%

SURFACE VISCOSITY OF PITCH FILMS^{*}

Hot water and hot alkaline extracts of Flambeau sulfite pulp were prepared, and varying amounts of calgon and/or alum were injected into the extracts. Film formation and viscosity were observed at different pH's. Other experiments were run using a benzene -95% ethanol (2:1) extract of Flambeau pulps spread on calgon and/or alum substrates. From the data summarized in Tables II, III, and IV, it appears that the addition of calgon does not appreciably effect the film viscosity. The presence of aluminum ion gives a solid, rigid type film.

^{*} This work was a continuation of experiments begun and reported in Project Report 2. (2).

TABLE II

THE EFFECT OF ALUMINUM ION ON PITCH FILM VISCOSITY

Substrate	Aluminum ion concentration	pH*	Film Viscosity in one hour-Boat Test (2)
Hot alkaline extract	$10^{-5}\underline{\text{M}}$	2.8	gaseous-liquid
		5.2	gaseous-liquid
		7.4	solid
		11.6	gaseous-liquid
Hot water extract	$10^{-5}\underline{\text{M}}$	3.1	liquid
		4.8	gaseous-liquid
		7.2	solid
		11.5	gaseous-liquid
Hot alkaline extract	$10^{-4}\underline{\text{M}}$	2.5	liquid
		5.7	solid
		7.2	solid
		10.4	gaseous-liquid
Hot water extract	$10^{-4}\underline{\text{M}}$	2.8	gaseous-liquid
		5.0	solid
		7.0	solid
		10.1	gaseous-liquid
Hot alkaline extract	$3 \times 10^{-4}\underline{\text{M}}$	3.0	solid
		5.5	solid
		7.1	solid
		7.8	gaseous-liquid
		11.6	gaseous-liquid
Hot water extract	$3 \times 10^{-4}\underline{\text{M}}$	2.9	solid
		4.9	solid
		6.9	gaseous-liquid
		7.3	gaseous-liquid
		9.3	liquid

*The pH was adjusted either with hydrochloric acid or sodium hydroxide.

THE EFFECT OF CALGON ON PITCH FILM VISCOSITY

Substrate	Calgon concentration	pH*	Film Viscosity in one hour-Boat Test (2),
Hot alkaline extract	$8 \times 10^{-6} \underline{\text{M}}$	2.0	gaseous-liquid
		2.5	gaseous-liquid
		6.5	gaseous-liquid
		8.0	gaseous-liquid
		10.5	gaseous-liquid
Hot water extract	$8 \times 10^{-6} \underline{\text{M}}$	2.2	gaseous-liquid
		2.5	gaseous-liquid
		6.6	gaseous-liquid
		6.8	gaseous-liquid
		10.5	gaseous-liquid
Hot alkaline extract	$10^{-5} \underline{\text{M}}$	11.0	gaseous-liquid
		2.9	gaseous
		6.9	gaseous-liquid
		8.1	gaseous-liquid
		10.3	gaseous-liquid
Hot water extract	$10^{-5} \underline{\text{M}}$	2.4	gaseous-liquid
		6.0	gaseous-liquid
		7.2	gaseous-liquid
		10.1	gaseous-liquid
Hot alkaline extract	$10^{-4} \underline{\text{M}}$	2.8	gaseous-liquid
		6.6	gaseous-liquid
		7.7	gaseous-liquid
		10.3	gaseous-liquid
Hot water extract	$10^{-4} \underline{\text{M}}$	2.8	gaseous-liquid
		6.0	gaseous-liquid
		7.1	gaseous-liquid
		10.4	gaseous-liquid

* The pH was adjusted either with hydrochloric acid or sodium hydroxide.

TABLE IV

THE EFFECT OF CALGON AND ALUMINUM ION ON PITCH FILM VISCOSITY

Substrate		Source of Pitch Film	Elapsed time, minutes	Aluminum ion Concentration	Viscosity of Control Containing only Aluminum ion	Aluminum ion and calgon	
	* pH				Boat test (2)	Calgon Concentration	Viscosity Boat test (2)
Hot alkaline extract	9.5	hot alkaline extract	15	$3 \times 10^{-4} \underline{M}$	gaseous-liquid	none	gaseous-liquid
			30		gaseous-liquid	$8 \times 10^{-6} \underline{M}$	gaseous-liquid
			45		gaseous-liquid	$2 \times 10^{-5} \underline{M}$	gaseous-liquid
			60		gaseous-liquid	$2 \times 10^{-5} \underline{M}$	gaseous-liquid
Hot alkaline extract	8.8	hot alkaline extract	15	$3 \times 10^{-4} \underline{M}$	gaseous-liquid	none	gaseous-liquid
			30		solid	$8 \times 10^{-6} \underline{M}$	gaseous-liquid
			30		solid	$2 \times 10^{-5} \underline{M}$	gaseous-liquid
			45		solid	$2 \times 10^{-5} \underline{M}$	solid
Hot alkaline extract	9.3	hot alkaline extract	15	$3 \times 10^{-4} \underline{M}$	gaseous-liquid	none	gaseous-liquid
			30		solid	$8 \times 10^{-6} \underline{M}$	liquid-solid
			40		solid	$2 \times 10^{-5} \underline{M}$	solid
			55		solid		solid
Hot water extract	7.2	hot water extract	15	$3 \times 10^{-4} \underline{M}$	liquid	none	liquid
			30		liquid	none	liquid
			45		liquid-solid	$8 \times 10^{-6} \underline{M}$	liquid-solid
			60		liquid-solid	$2 \times 10^{-5} \underline{M}$	liquid-solid
Hot water extract	6.8	hot water extract	15	$3 \times 10^{-4} \underline{M}$	gaseous-liquid	none	gaseous-liquid
			30		gaseous-liquid	none	gaseous-liquid
			45		gaseous-liquid	$8 \times 10^{-6} \underline{M}$	gaseous-liquid
			60		gaseous-liquid	$2 \times 10^{-5} \underline{M}$	gaseous-liquid
			75		liquid		
Distilled water	4.8	benzene-95% ethanol	15	$10^{-4} \underline{M}$	--	none	liquid

Collection of Pitch Film

The apparatus, the preparation of the pulp extract, and the method of film collection are described in Project Report 2 (2).

The pH's of the pulp slurries were adjusted either with sodium hydroxide or hydrochloric acid. The extracts were spread on a distilled water substrate containing 10^{-4} M aluminum ion.

An approximate fiber analysis of Interlake Mill pulp showed the pulp to be an unbleached, medium cooked 100% spruce sulfite, whereas the Flambeau pulp was 75% softwood sulfite (spruce, also some hemlock), 25% hardwood sulfite (aspen and birch).

A study of the pitch films obtained from extracts at different pH's is given in Table V. As the extract pH was lowered the film became less rigid and the amount of film collected was less. Because it was necessary to collapse and collect many films for an analysis, fractionation was not shown.

Table V also gives the composition of a benzene -95% ethanol (2:1) extract of Interlake Mill pulp.

To test the reliability of the analytical determination for resin acids, fatty acids, and unsaponifiabiles, a known mixture containing abietic acid, stearic acid, and the unsaponifiable fraction from the benzene -95% ethanol extract was prepared. The total recovery was 95%. The data are given in Table V.

SURFACE BALANCE STUDIES OF PITCH AND ITS COMPONENTS.

A series of surface balance studies were made both on whole pitch, obtained from a benzene -95% ethanol (2+1) extract of sulfite pulp, and the fatty acid, resin acid, and unsaponifiable fractions isolated in an analytical determination (Table V) of the benzene-alcohol extract. The fatty acid esters were hydrolyzed to fatty acids.

A Cenco hydrophil balance was attached to a plexi-glass trough, 30 inches x 5-7/8 inches x 1/2 inch, which was mounted on a marble slab. The apparatus was enclosed in a plexi-glass case. A motor driven, constant speed barrier was used to compress or decompress the films. The edges of the trough were covered with teflon tape, and the barrier was coated with fresh paraffin wax. Readings were recorded while the barrier was moving. The only time the machine was stopped was to allow the gears to reverse directions.

A study of the effect of pH, aluminum ion and calgon on films from whole pitch and its components was made. Data obtained from the films are given in the appendix, Tables VII-XXVIII. Pressure-area curves were drawn, Figures 1-21. Table VI lists the properties of the films formed on various substrates.

Apparently, on the alkaline and the calgon substrates salts are formed of the fatty and resin acids, and they dissolve into the substrate. In this way the number of grams of fatty and resin acids used to compute the area per gram is not the true value. This effect would account for the highly compressible curves and the low extrapolated area values.

The formula for compressibility and methods of reporting surface pressure-area information are in the literature (3, 4, 5, 6)

Key for Table VI

A_0 area where first increase in pressure occurs

A_1 area at 1 dyne per cm.

A_{10} area at 10 dynes per cm.

A_{15} area at 15 dynes per cm.

A_{ext} the extrapolated area

$$\text{Compressibility } -k = \frac{1}{A} \left(\frac{dA}{d\pi} \right) \quad (4)$$

where k is the compressibility,

A is the area, and

π is the film pressure

TABLE VI
PROPERTIES OF FILMS

Substrate	Film	Area per gram x 10 ⁻⁵ , cm. ²					Area per molecule, o ₂ A extrapolated	Compressibility, cm. per dyne at 15 dynes per cm.
		A ₀	A ₁	A ₁₀	A ₁₅	A _{ext}		
Dilute hydrochloric acid, pH 2	Whole pitch	61	59	36	21	60	--	0.129
	Fatty acid	116	110	67	59	81	--	0.025
	Resin acid	--	--	54	43	75	36.9	0.037*, 0.186**
	Unsaponifiable	--	68	47	42	57	--	0.033
Distilled water, pH 6.3-6.5	Whole pitch	60	53	31	20	53	--	0.110
	Fatty acid	110	94	61	52	75	--	0.028
	Resin acid	64	55	32	24	48	23.9	0.066
	Unsaponifiable	70	65	48	42	63	--	0.036
Sodium hydroxide, pH 10-11	Whole pitch	72	50	32	22	51	--	0.082
	Fatty acid	30	--	16	13	21	--	0.031
	Resin acid	42	42-64	16	13	22	11.0	0.031
	Unsaponifiable	77	64	48	42	59	--	0.029
Distilled water containing 5 x 10 ⁻⁴ M aluminum ion, pH 4	Whole pitch	63	60	40	25	63	--	0.092
	Fatty acid	80	71	57	52	65	--	0.015
	Resin acid	--	--	55	50	63	31.4	0.018
	Unsaponifiable	--	68	50	43	65	--	0.033
Tap water containing 8 x 10 ⁻⁶ M Calgon pH 7.4-8.7	Whole pitch	67	56	36	25	55	--	0.076
	Fatty acid	110	96	53	45	64	--	0.029
	Resin acid	48	44	22	19	31	15.4	0.044
	Unsaponifiable	79	66	48	43	61	--	0.024

*Compressibility at 10 dynes per cm.

**Compressibility at 20 dynes per cm.

Figure 1

Film pressure-area curve for stearic acid spread on dilute hydrochloric acid pH 2.2, Temperature 21°C.

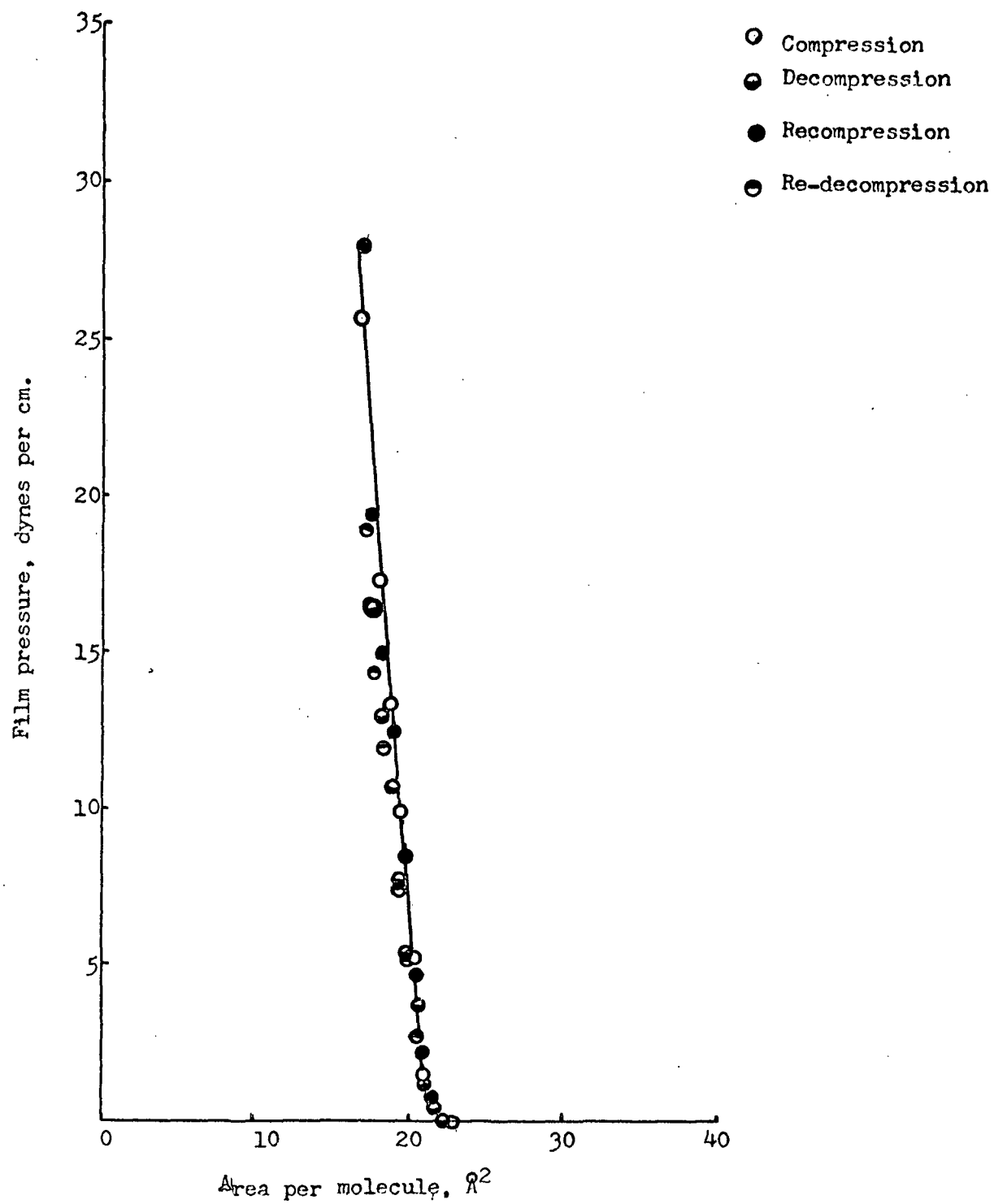


Figure 2

Film pressure-area curve for whole pitch spread on dilute hydrochloric acid. pH 1.7, Temperature 23°C.

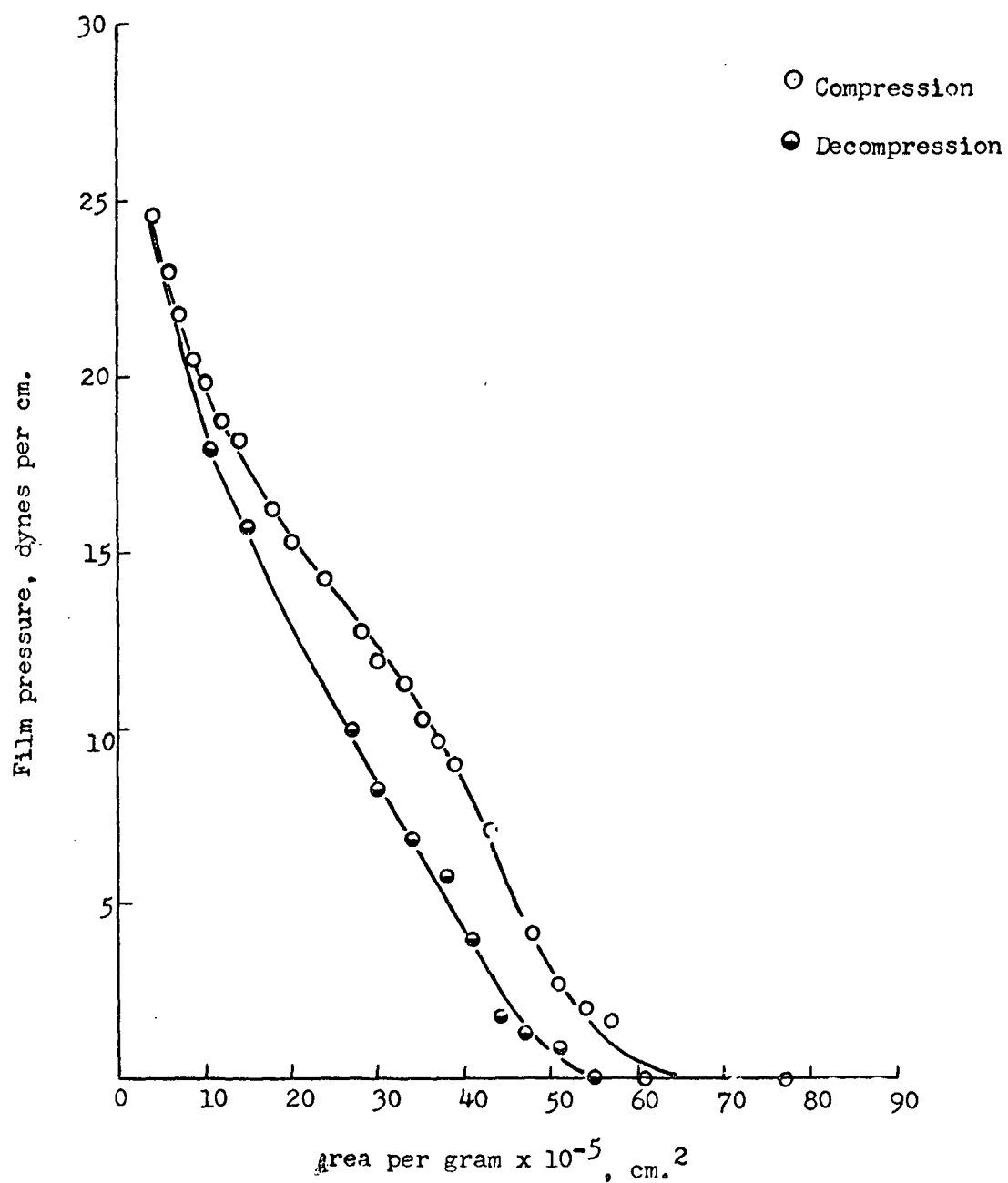
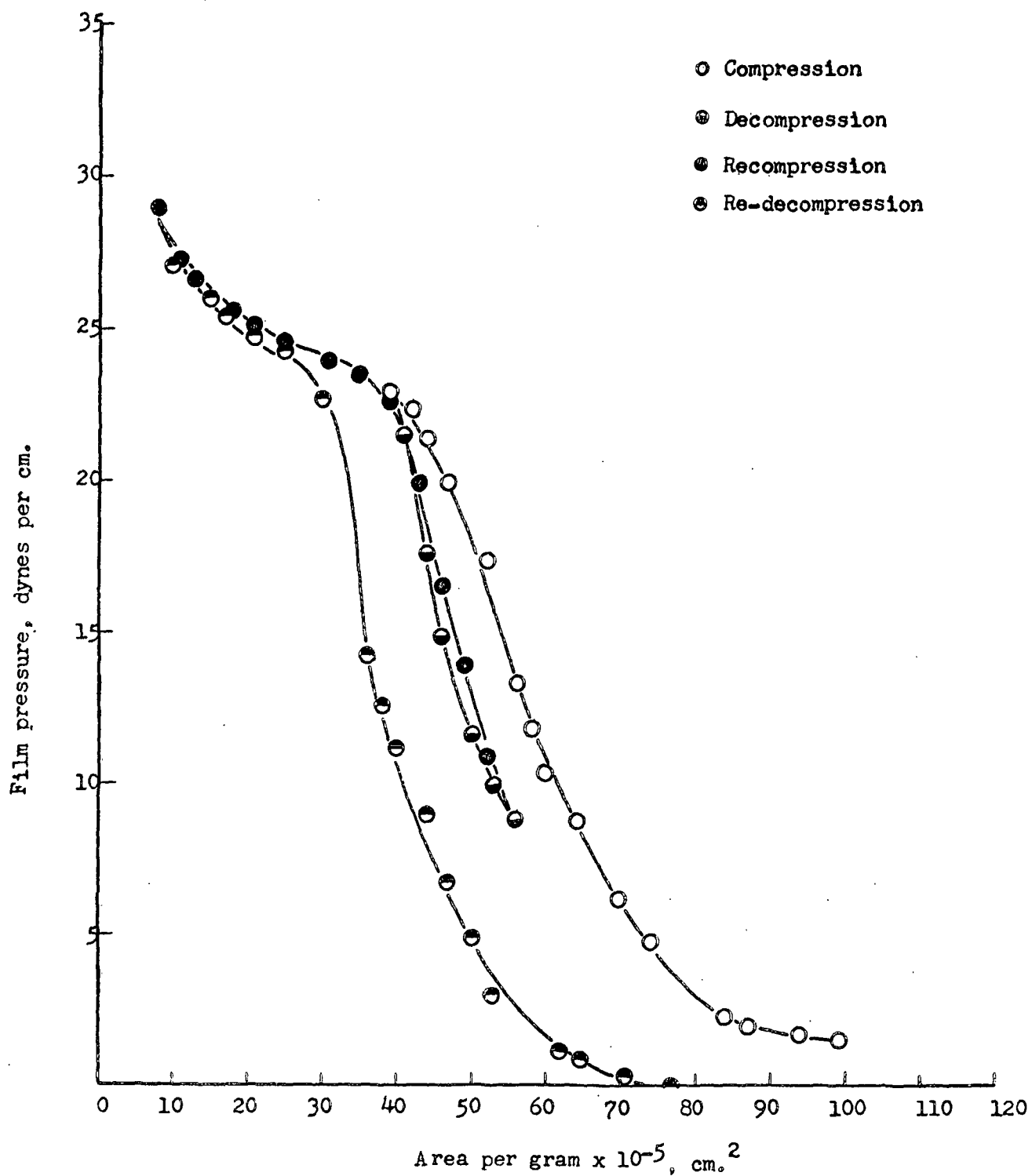


Figure 3

Film pressure-acid curve for fatty acid fraction spread on dilute hydrochloric acid, pH 2, Temperature 23°C.



Figuro 4

Film pressure-area curve for resin acid fraction spread on dilute hydrochloric acid. pH 1.5, Temperature 24°C.

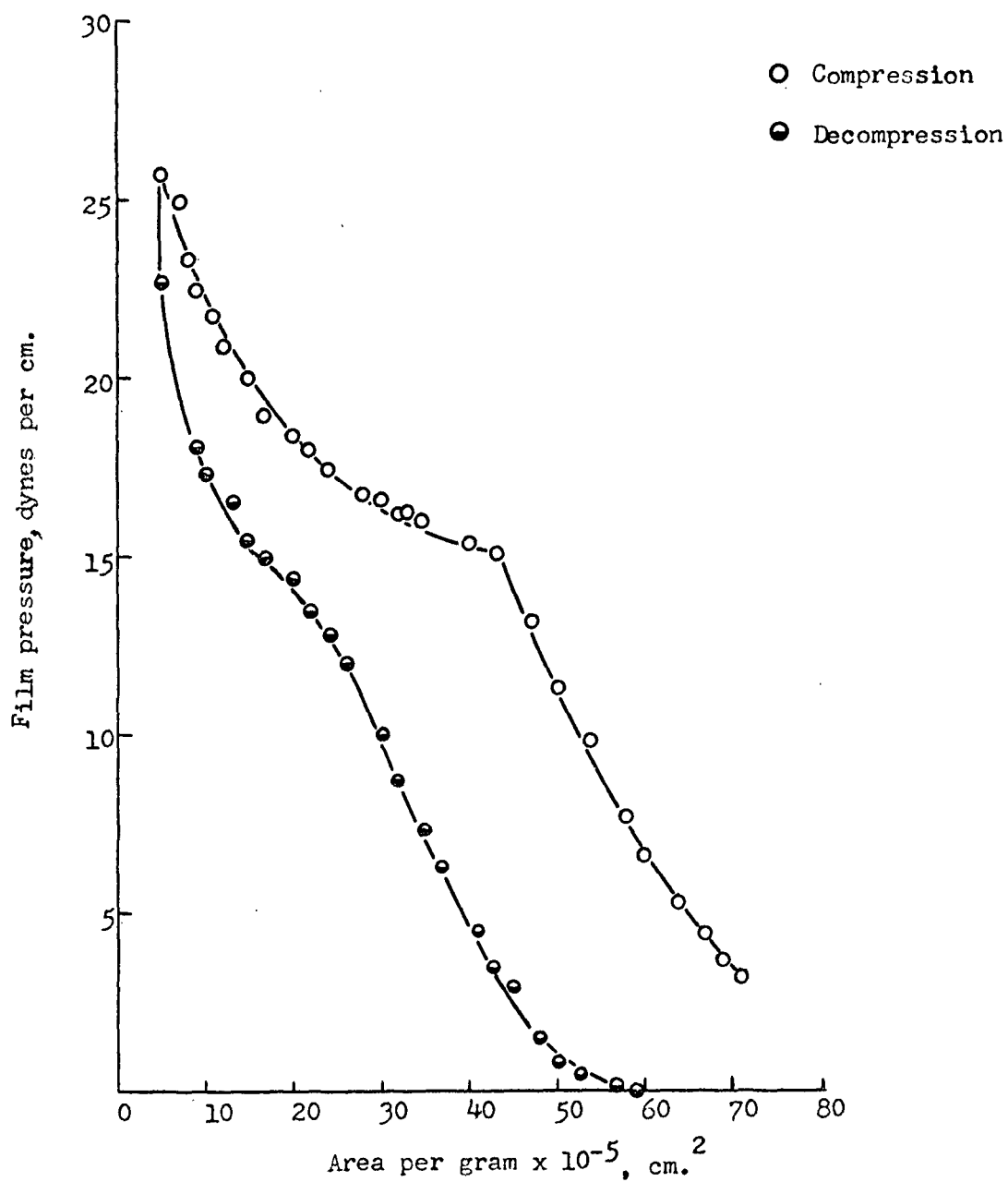


Figure 5

Film pressure-area curve for unsaponifiable fraction spread on dilute hydrochloric acid. pH 2. Temperature 21°C.

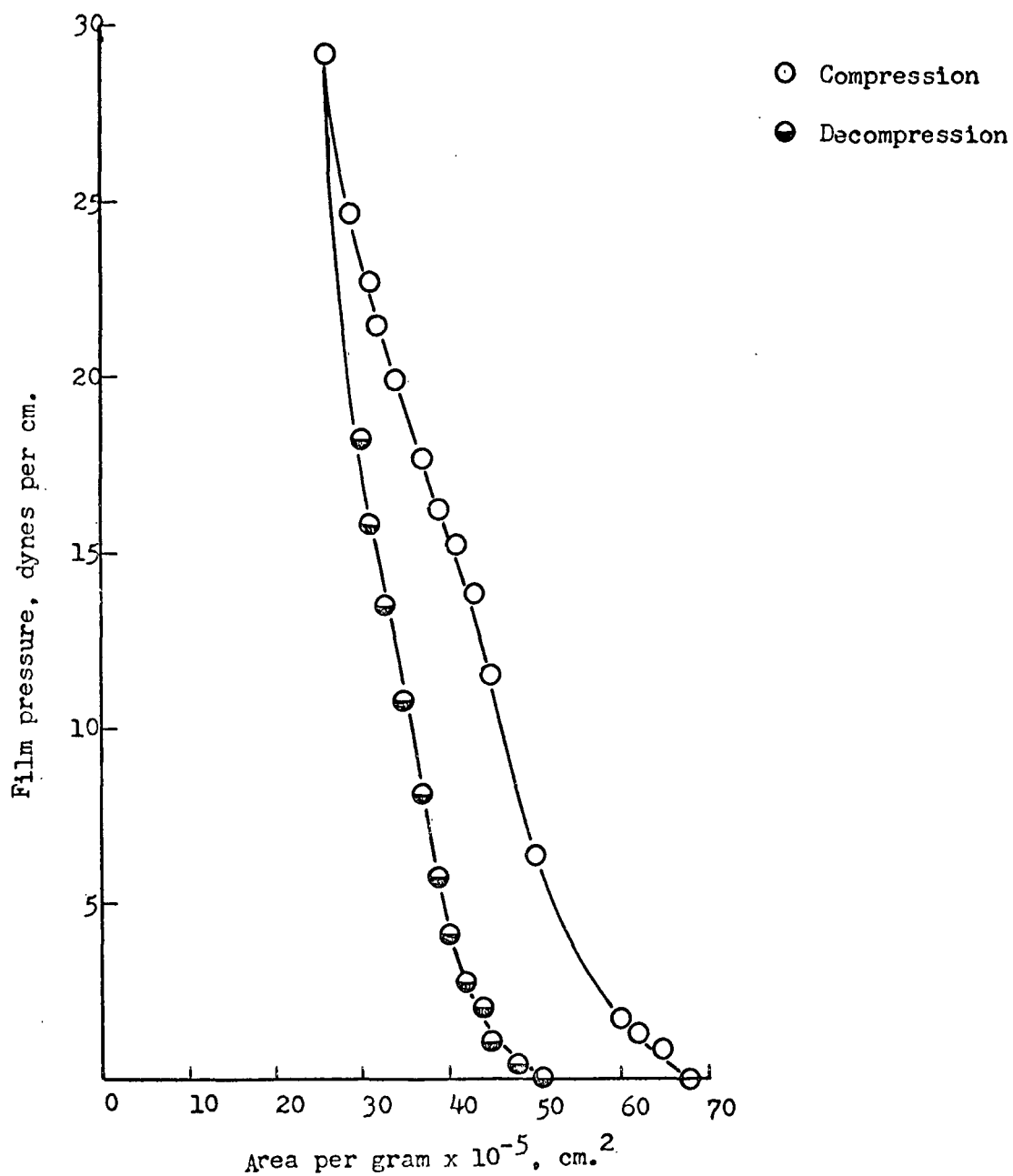


Figure 6

Film pressure-area curve for whole pitch spread on distilled water.
pH 6.3, Temperature 21.5° C.

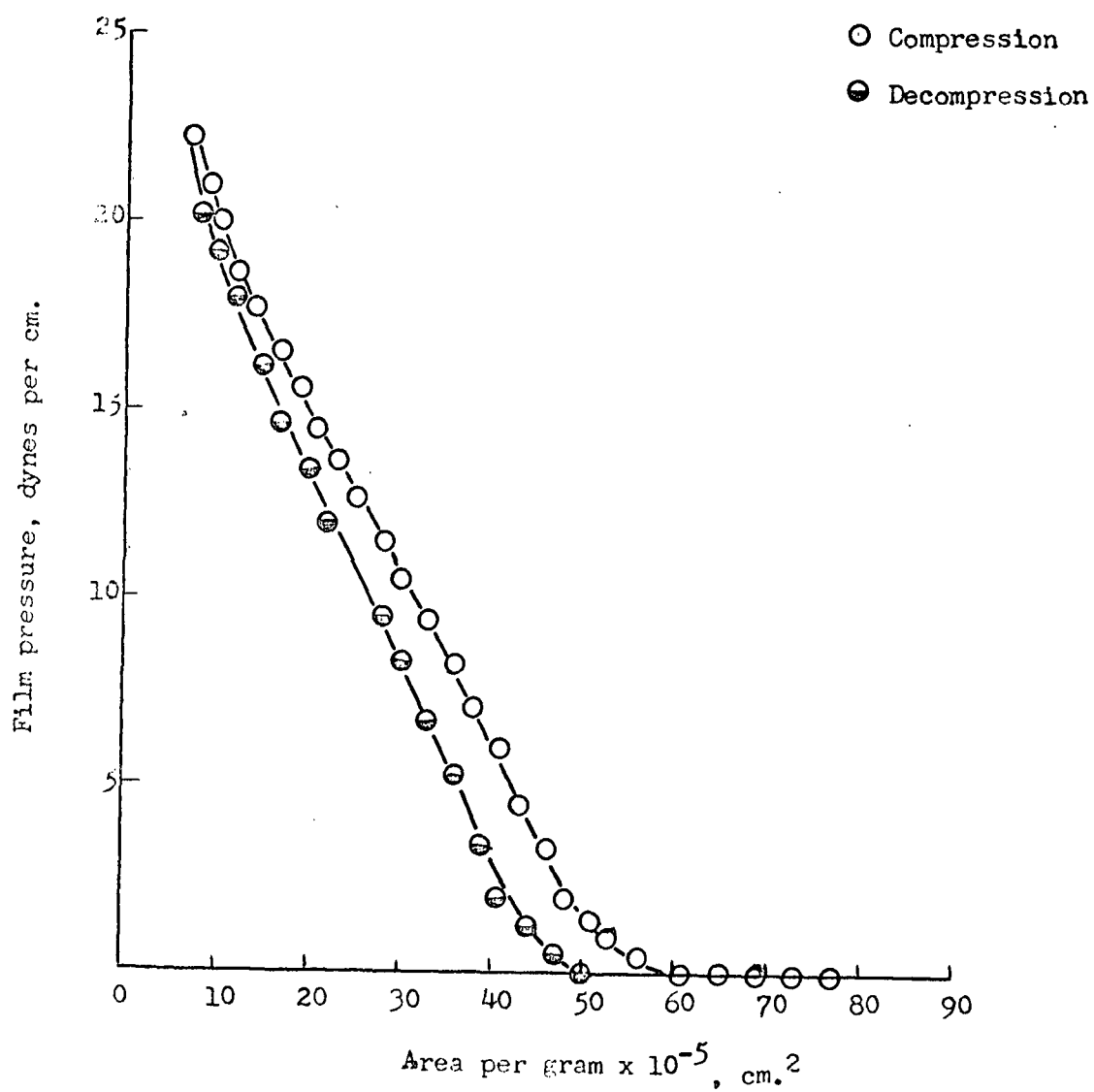


Figure 7

Film pressure-area curve for fatty acid fraction spread on distilled water. pH 6.5, temperature 21.5°C.

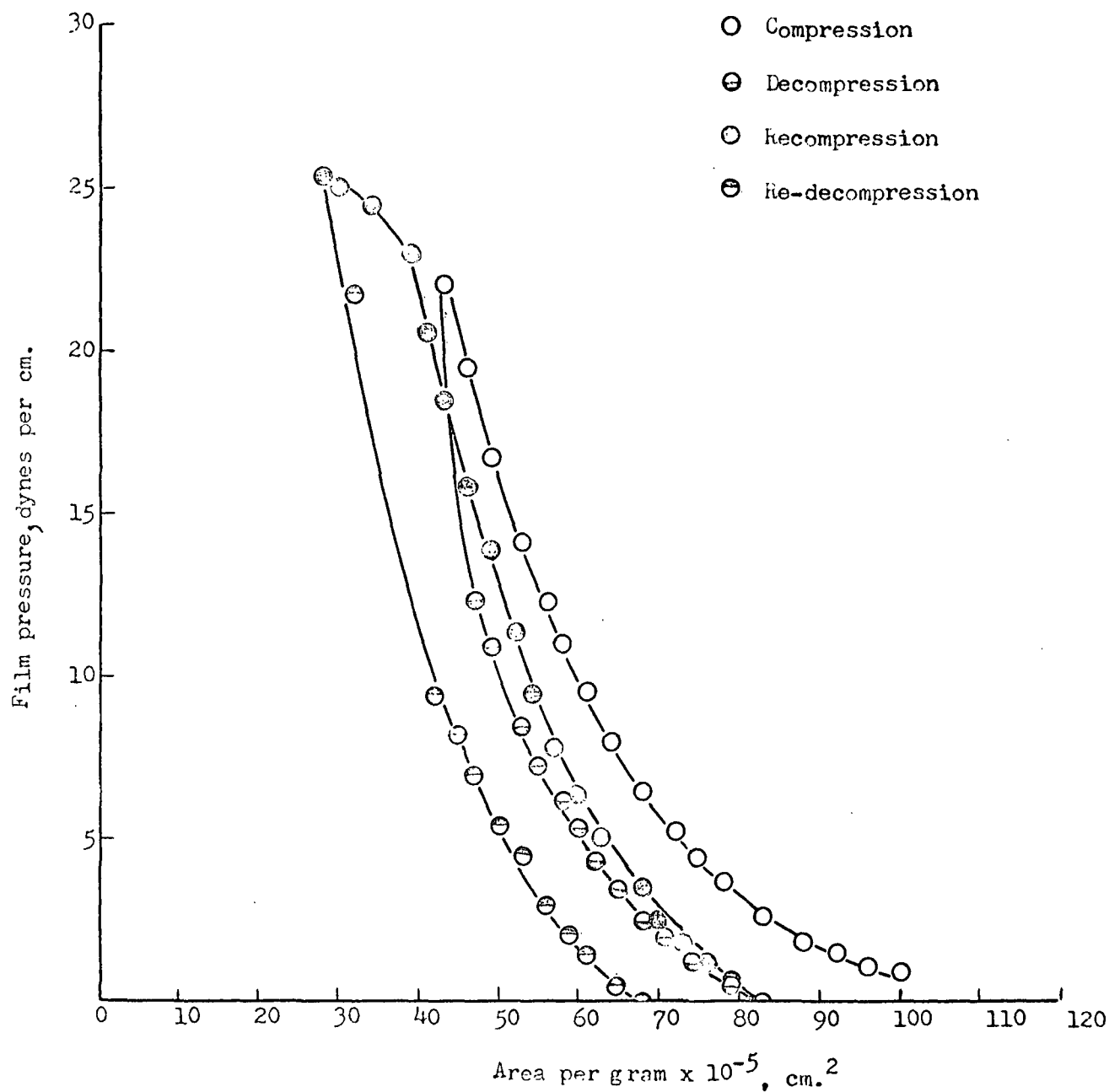


Figure 8

Film pressure-area curve for resin acid fraction spread on distilled water. pH 6.5, Temperature 21.5°C.

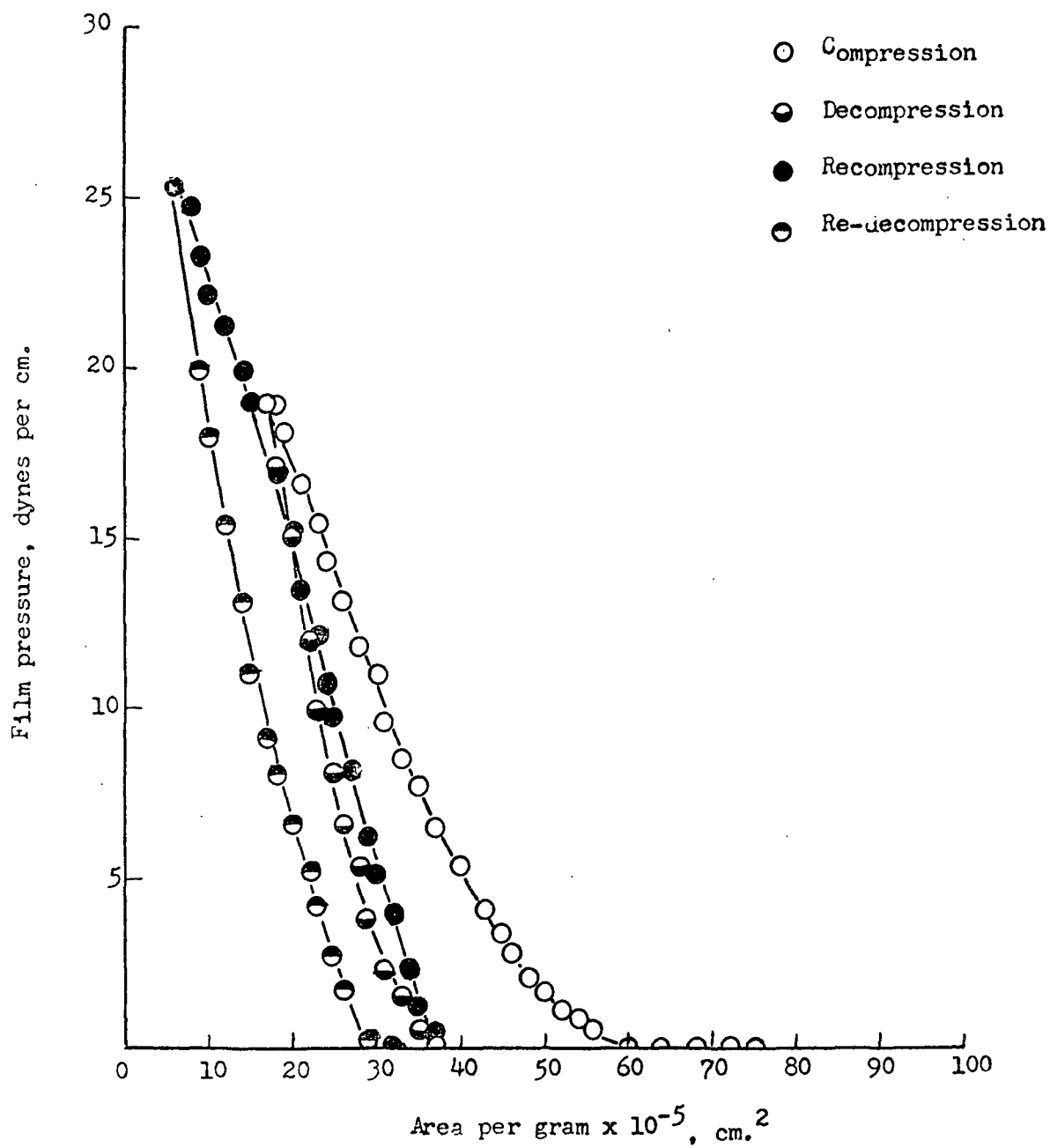


Figure 9

Film pressure-area curve for unsaponifiable fraction spread on distilled water. pH 6.5, Temperature 21.5°C.

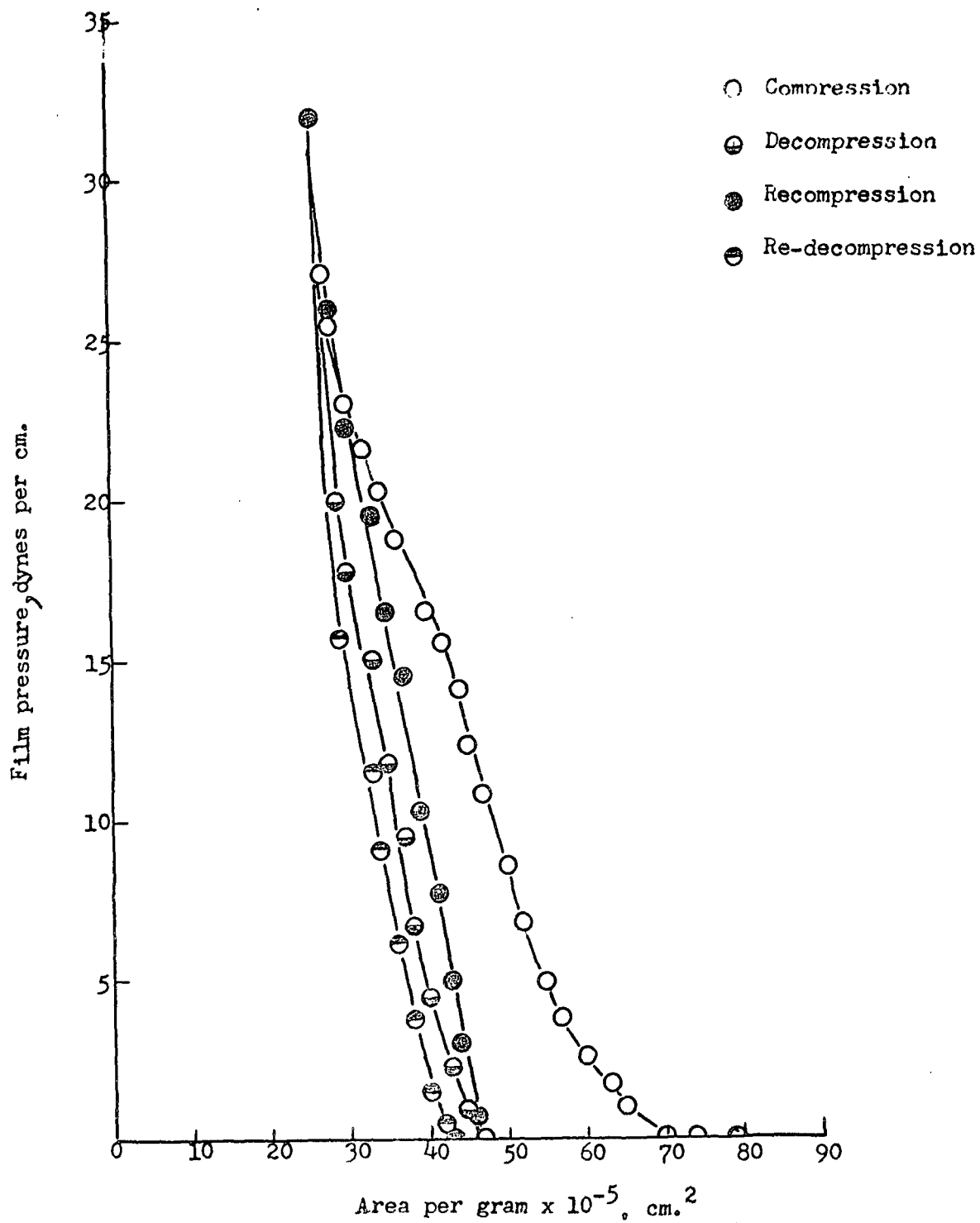


Figure 10

Film pressure-area curve for whole pitch spread on sodium hydroxide substrate. pH 11.3, Temperature 24.5°C.

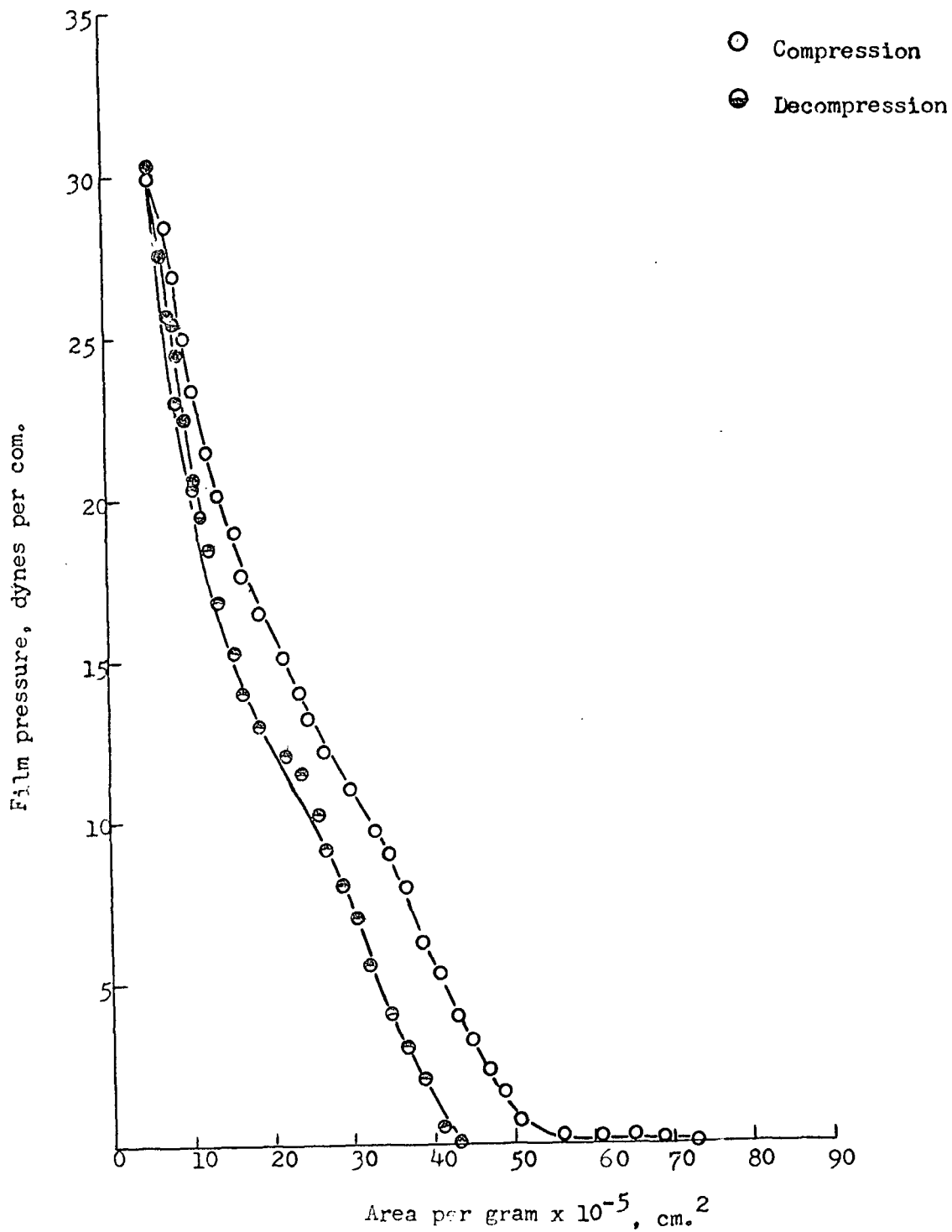


Figure 11

Film pressure-area curve for fatty acid fraction spread on sodium hydroxide substrate. pH 10.0, Temperature 23.5°C .

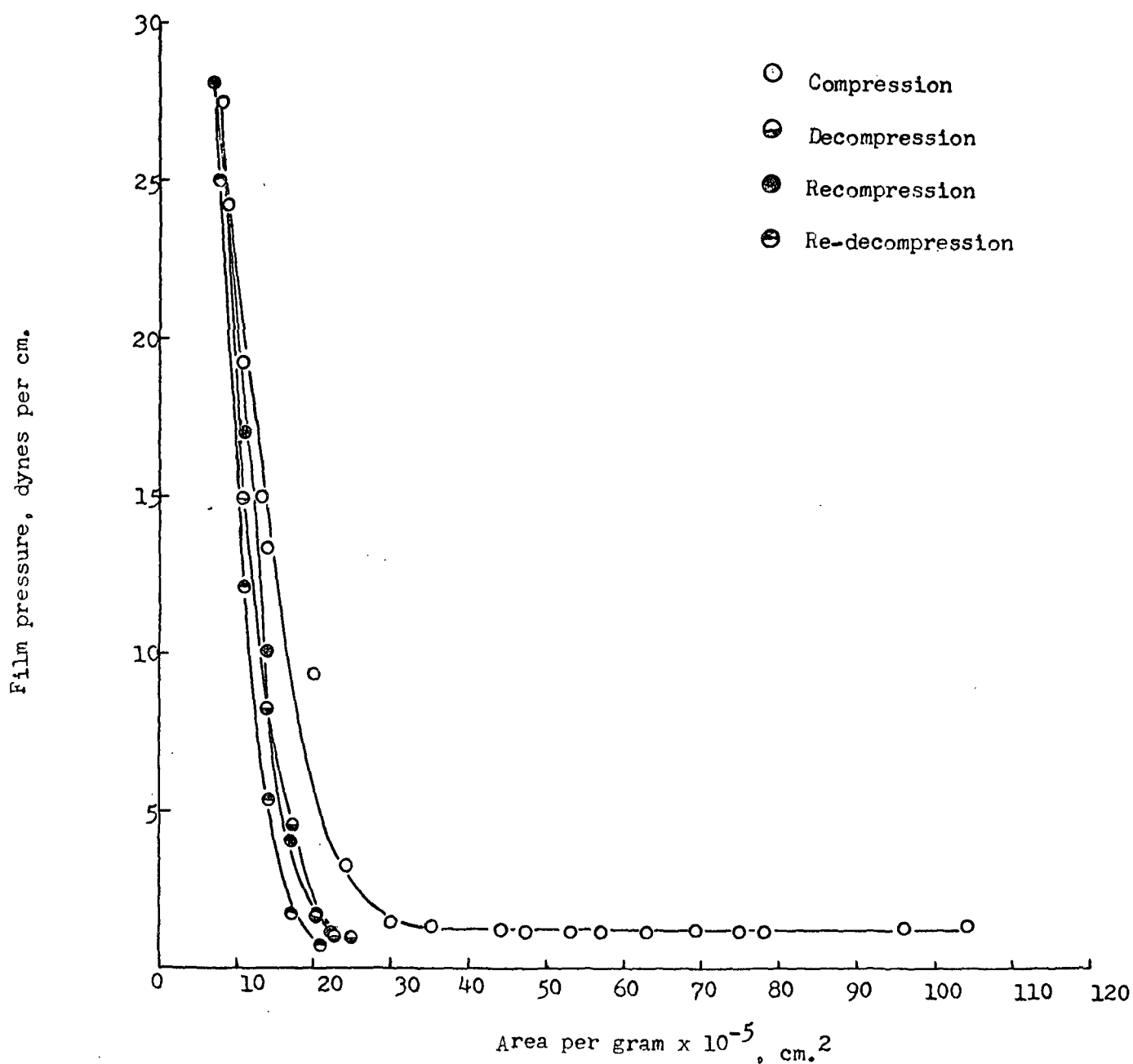


Figure 12

Film pressure-area curve for resin acid fraction spread on sodium hydroxide substrate. pH 11.0, Temperature 25°C.

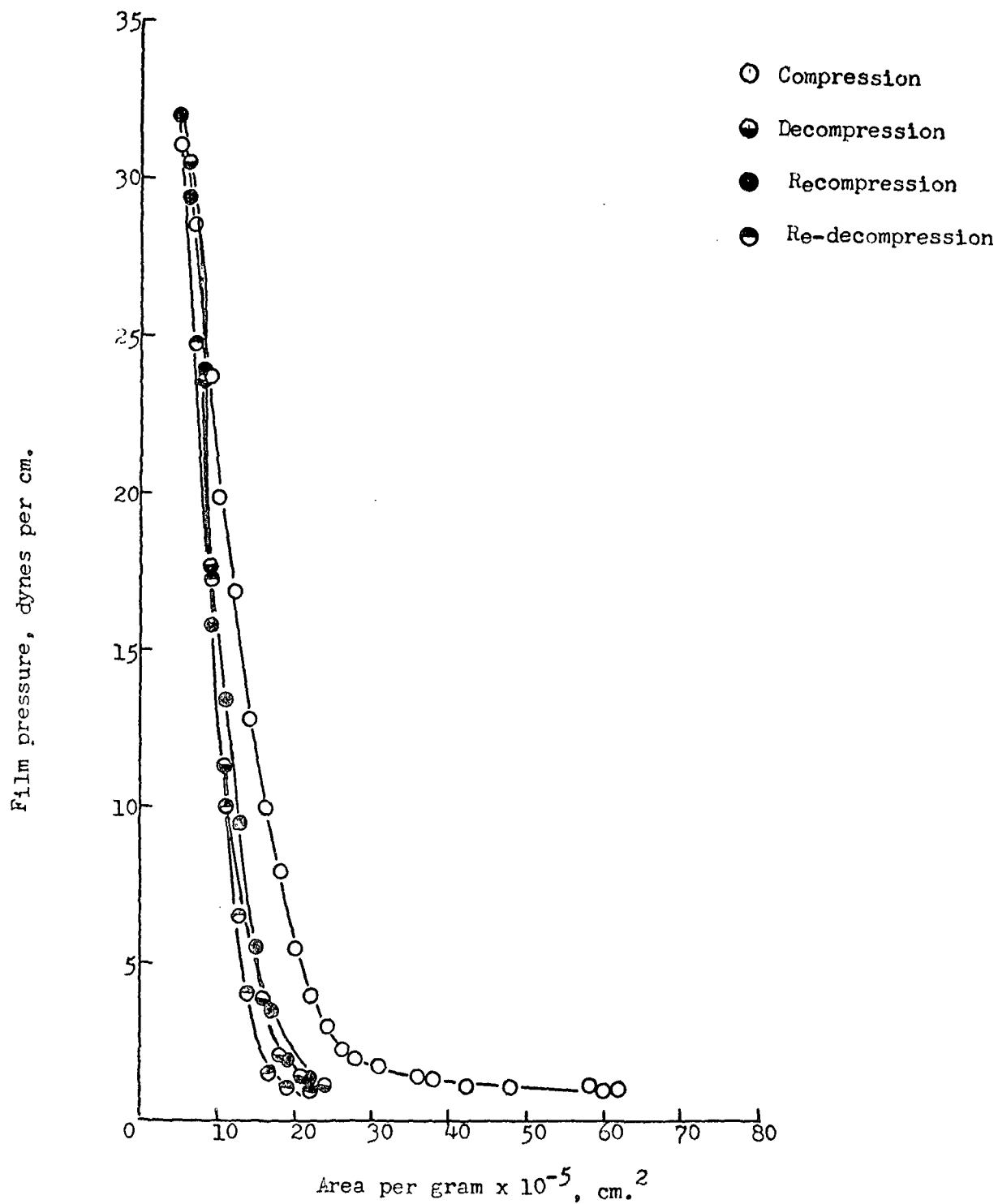


Figure 13

Film pressure-area curve for unsaponifiable fraction spread on sodium hydroxide substrate. pH 11.0, Temperature 25°C.

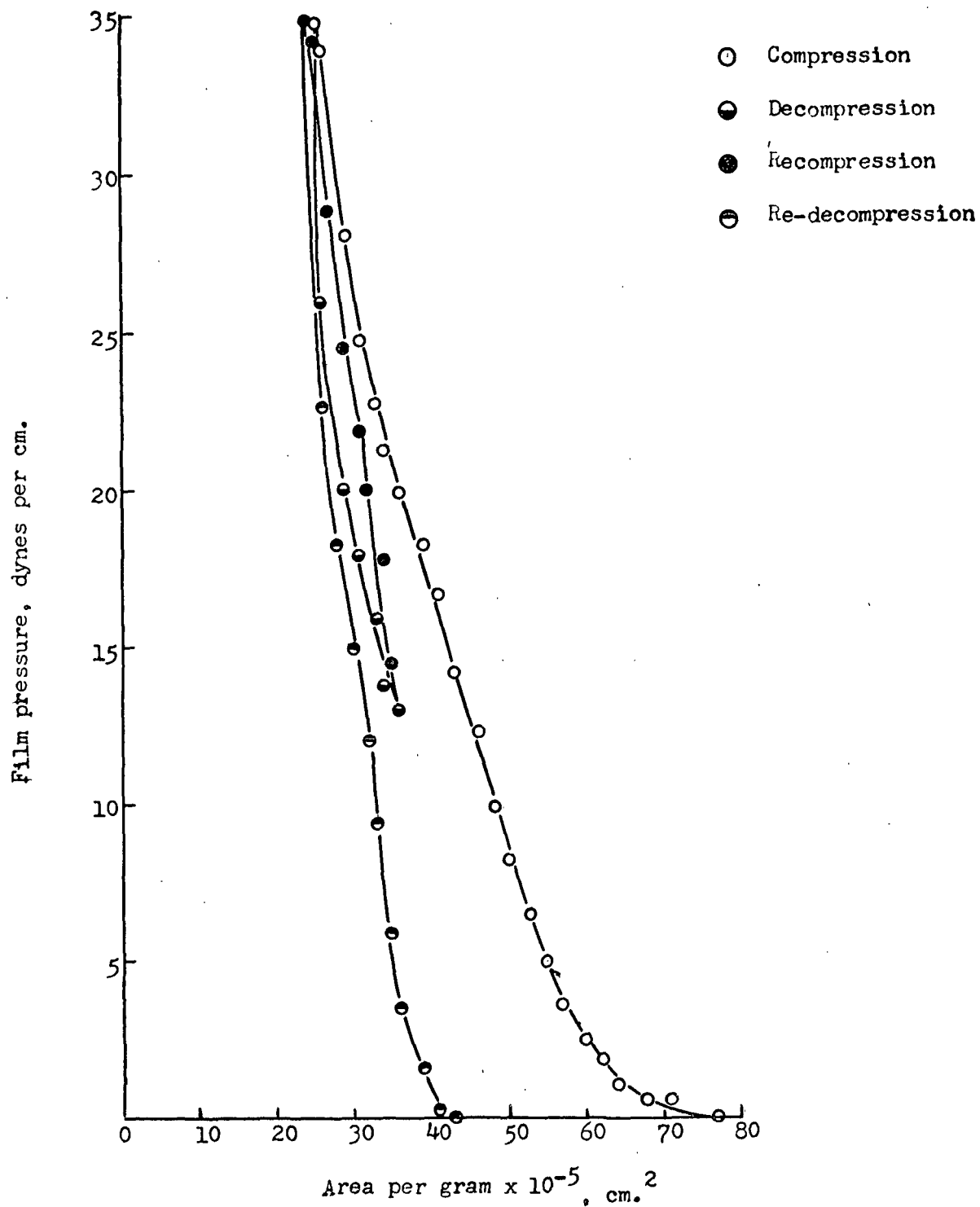


Figure 14

Film pressure-area curve for whole pitch spread on a distilled water substrate containing $5 \times 10^{-4} M$ aluminum ion. pH 4.1, Temperature $24^{\circ}C$.

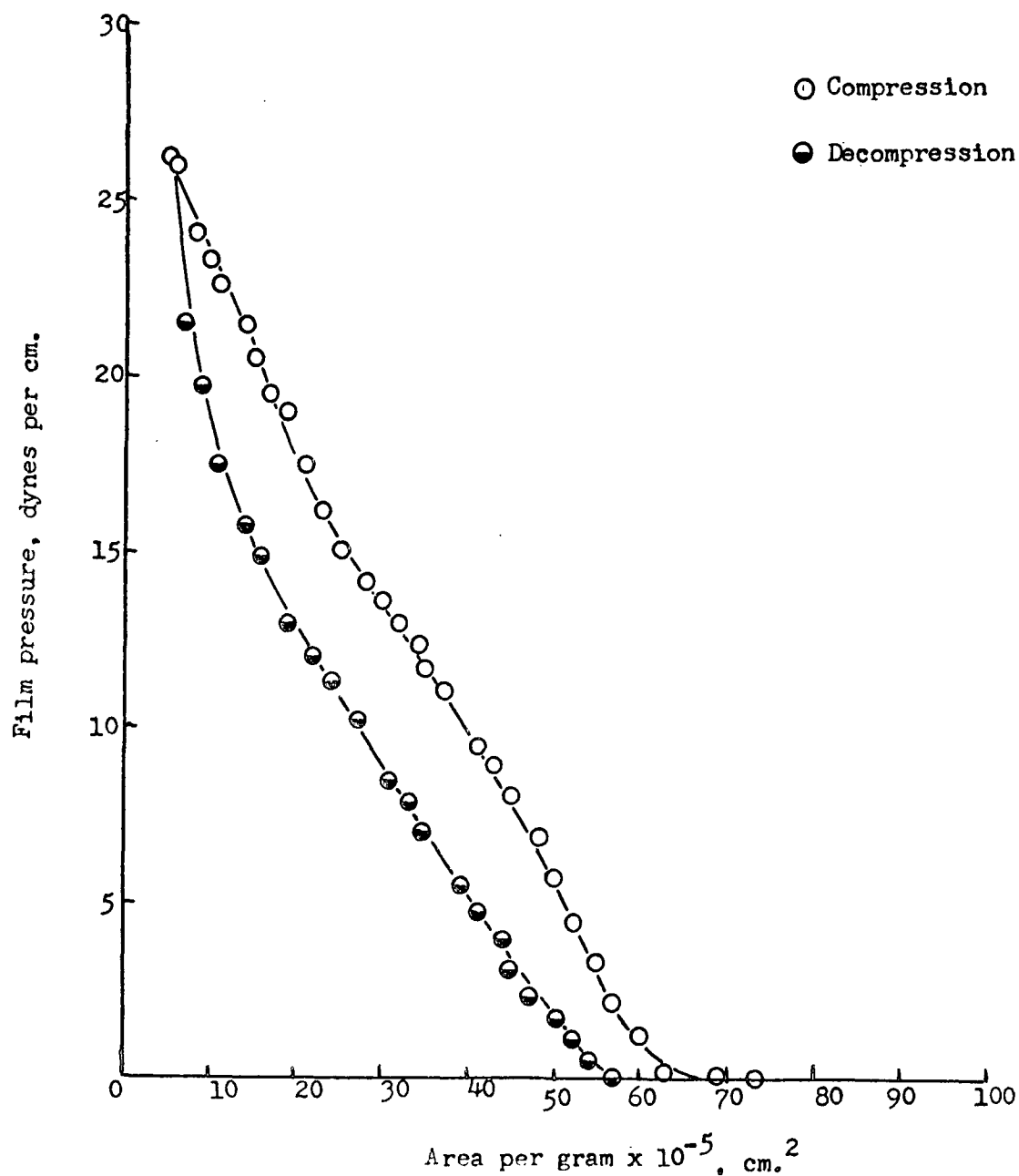


Figure 15

Film pressure-area curve for fatty acid fraction spread on a distilled water substrate containing $5 \times 10^{-4} M$ aluminum ion. pH 4.1, temperature $24^{\circ}C$.

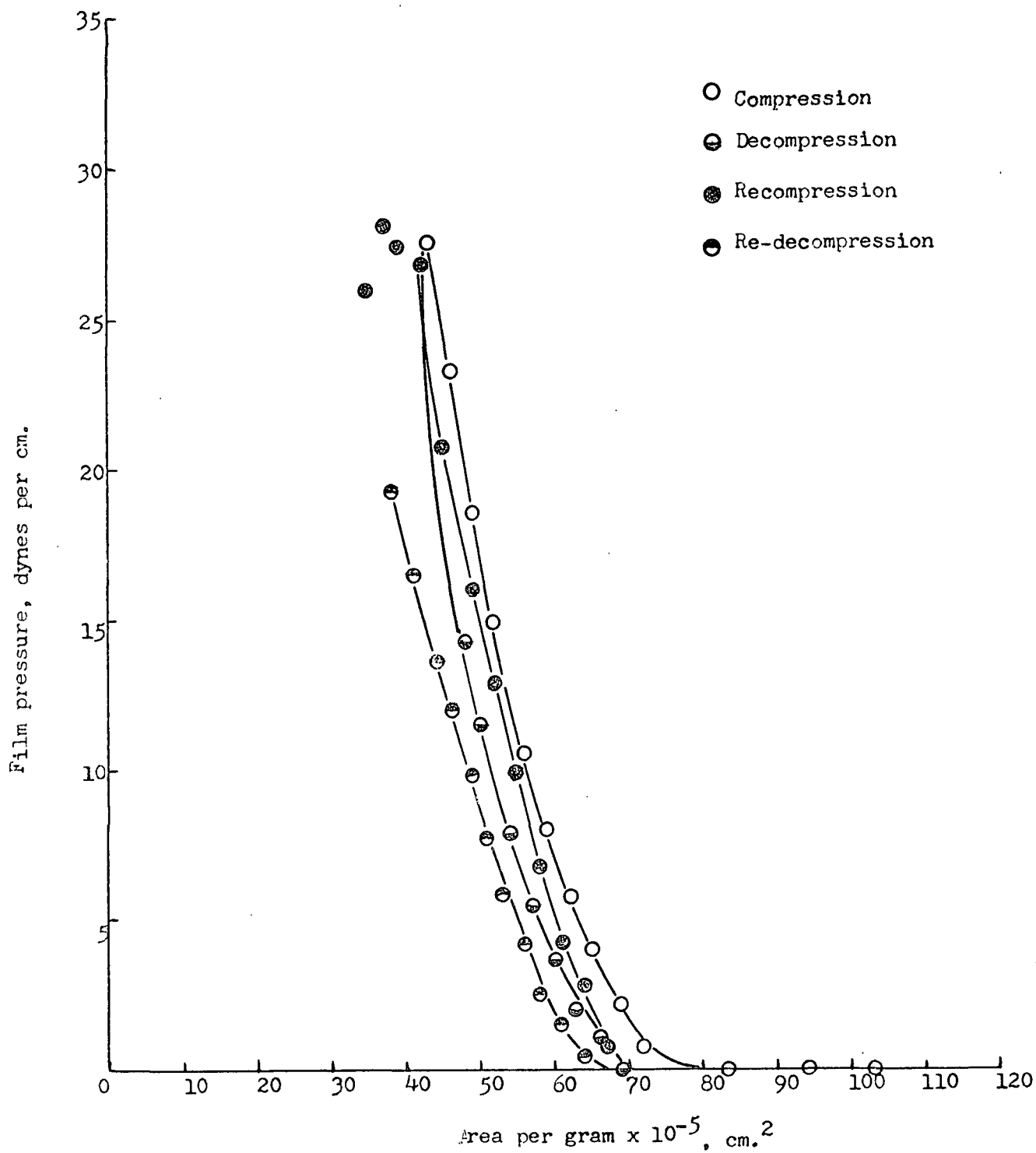


Figure 16

Film pressure-area curve for resin acid fraction spread on a distilled water substrate containing $5 \times 10^{-4} M$ aluminum ion. pH 4.1, Temperature $24^{\circ}C$.

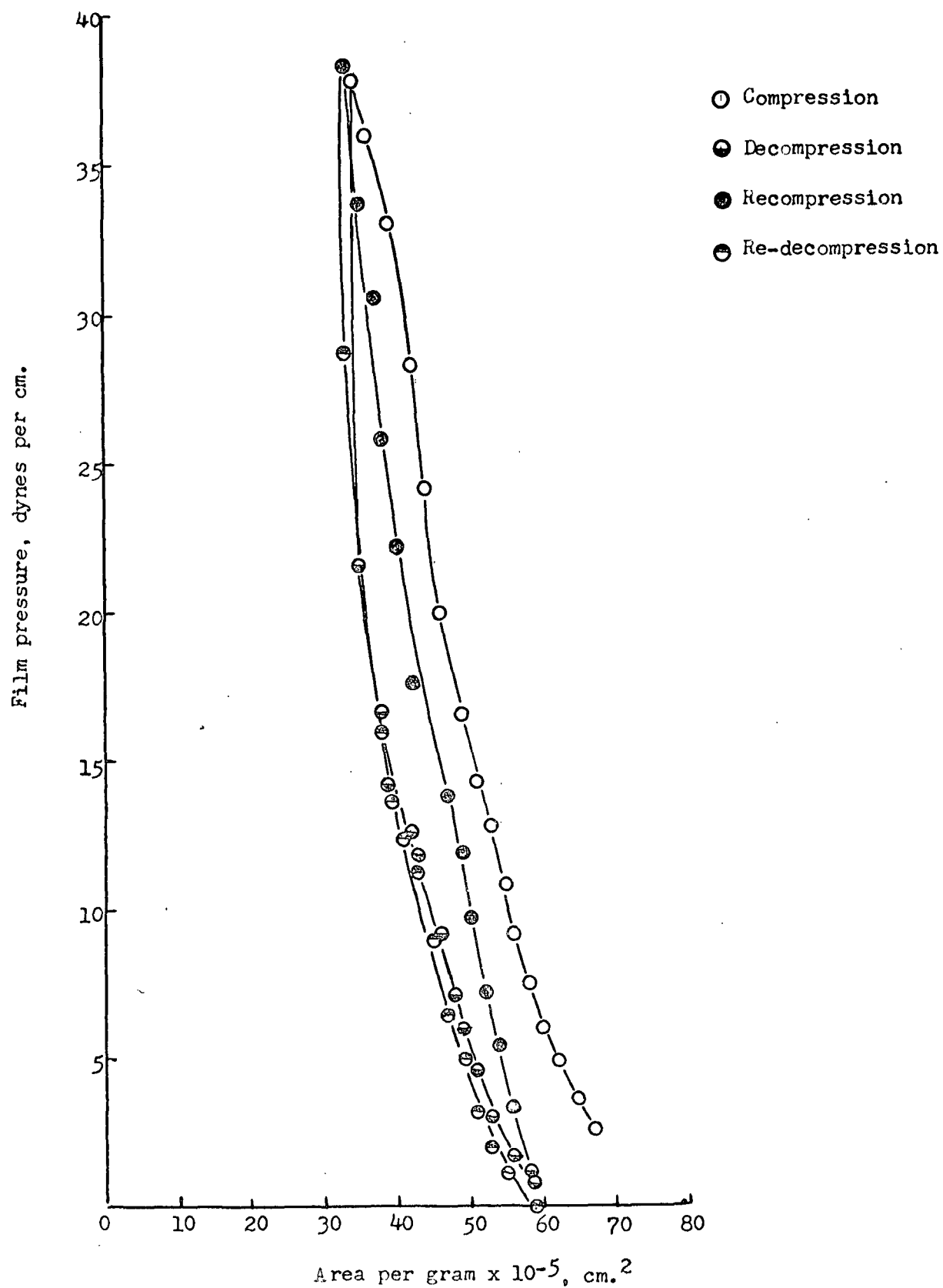


Figure 17

Film pressure-area curve for unsaponifiable fraction spread on a distilled water substrate containing $5 \times 10^{-4} M$ aluminum ion. pH 4.2, Temperature $21.5^{\circ}C$.

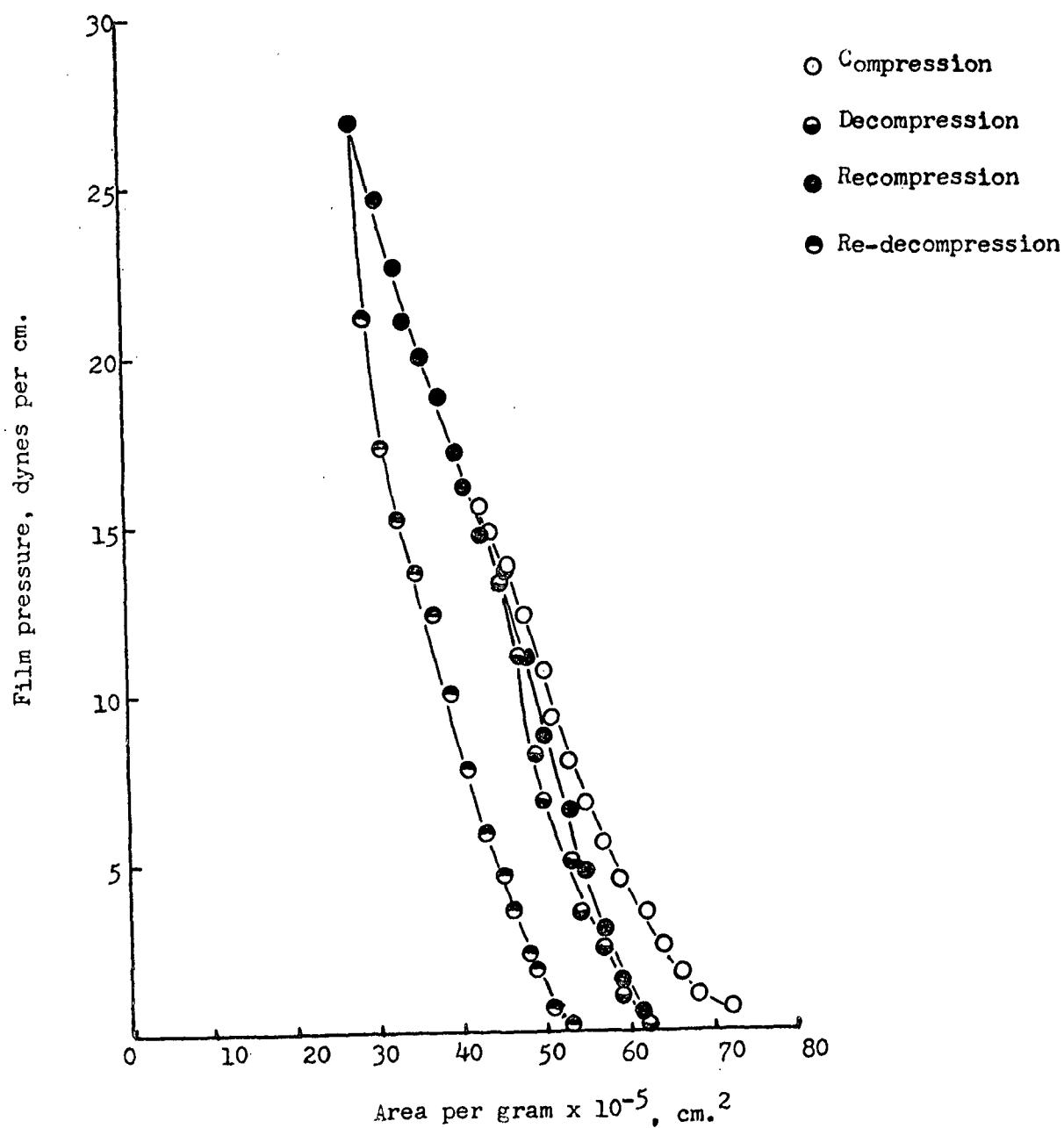


Figure 18

Film pressure-area curve for whole pitch spread on tap water containing 8×10^{-6} M calgon. pH 8.1, Temperature 25°C .

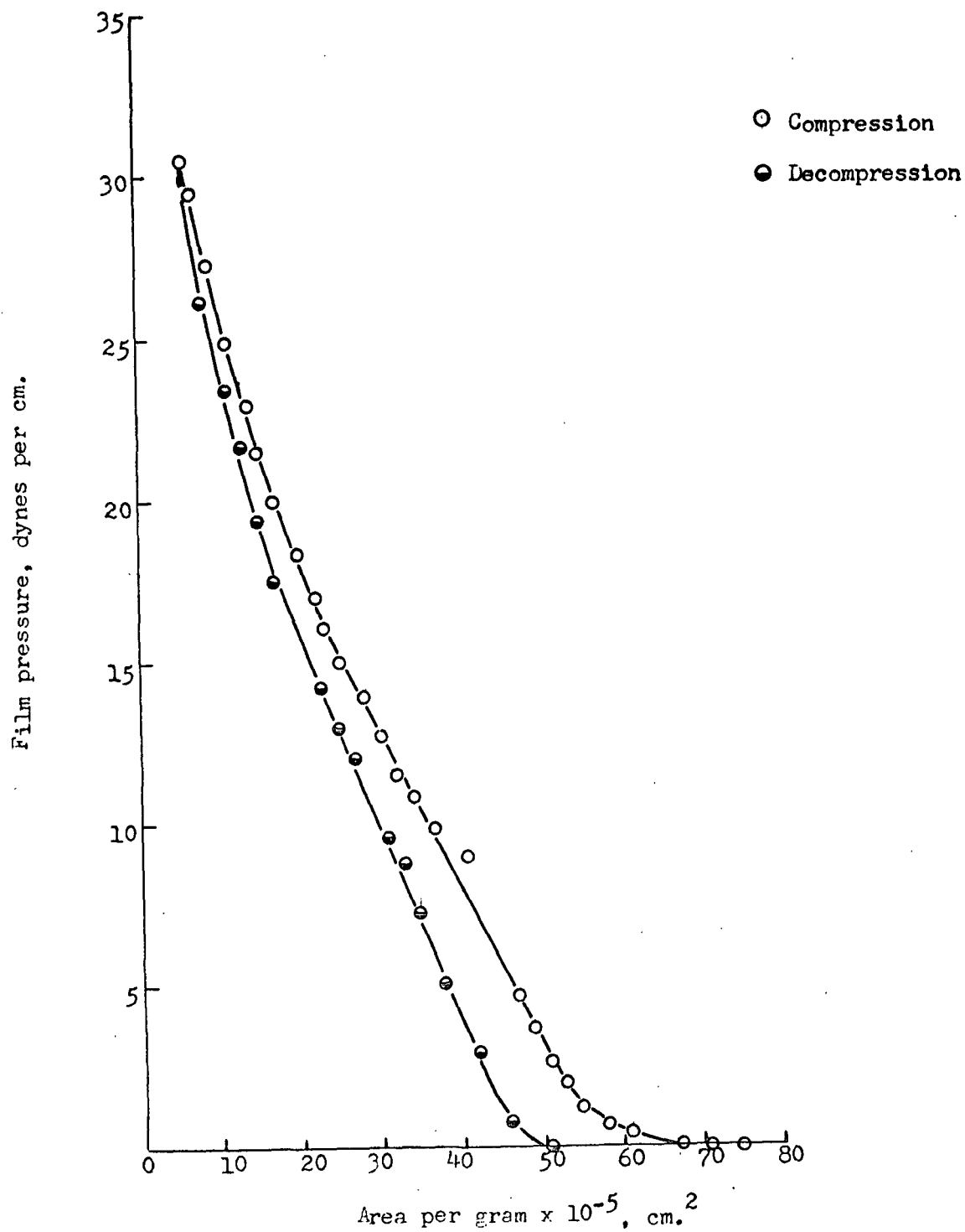


Figure 19

Film pressure-area curve for fatty acid fraction spread on tap water containing 8×10^{-6} M calgon. pH 8.7, Temperature 24.5°C .

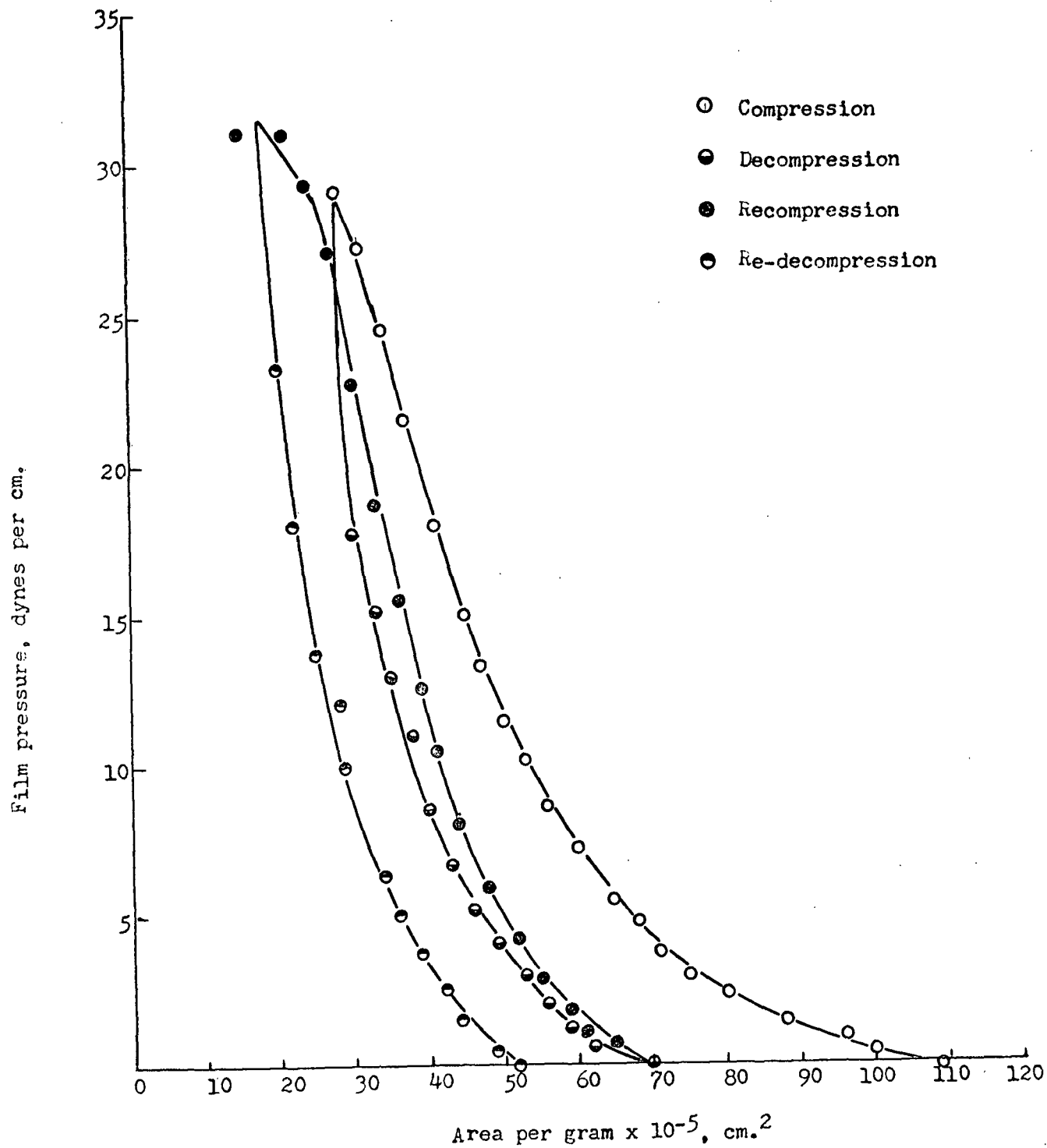


Figure 20

Film pressure-area curve for resin acid fraction spread on tap water containing $8 \times 10^{-6} \text{ M}$ calgon. pH 7.4, Temperature 25°C .

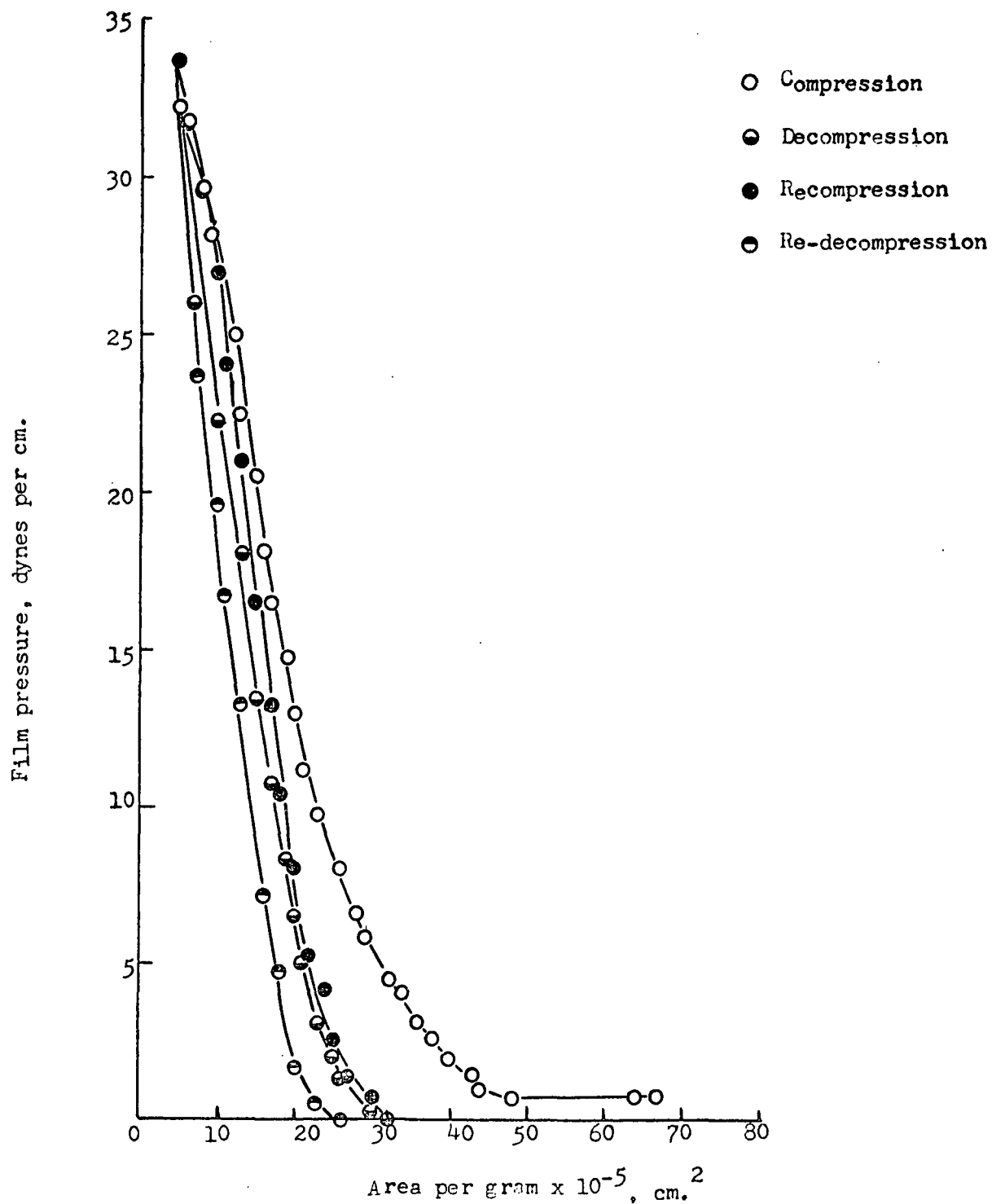
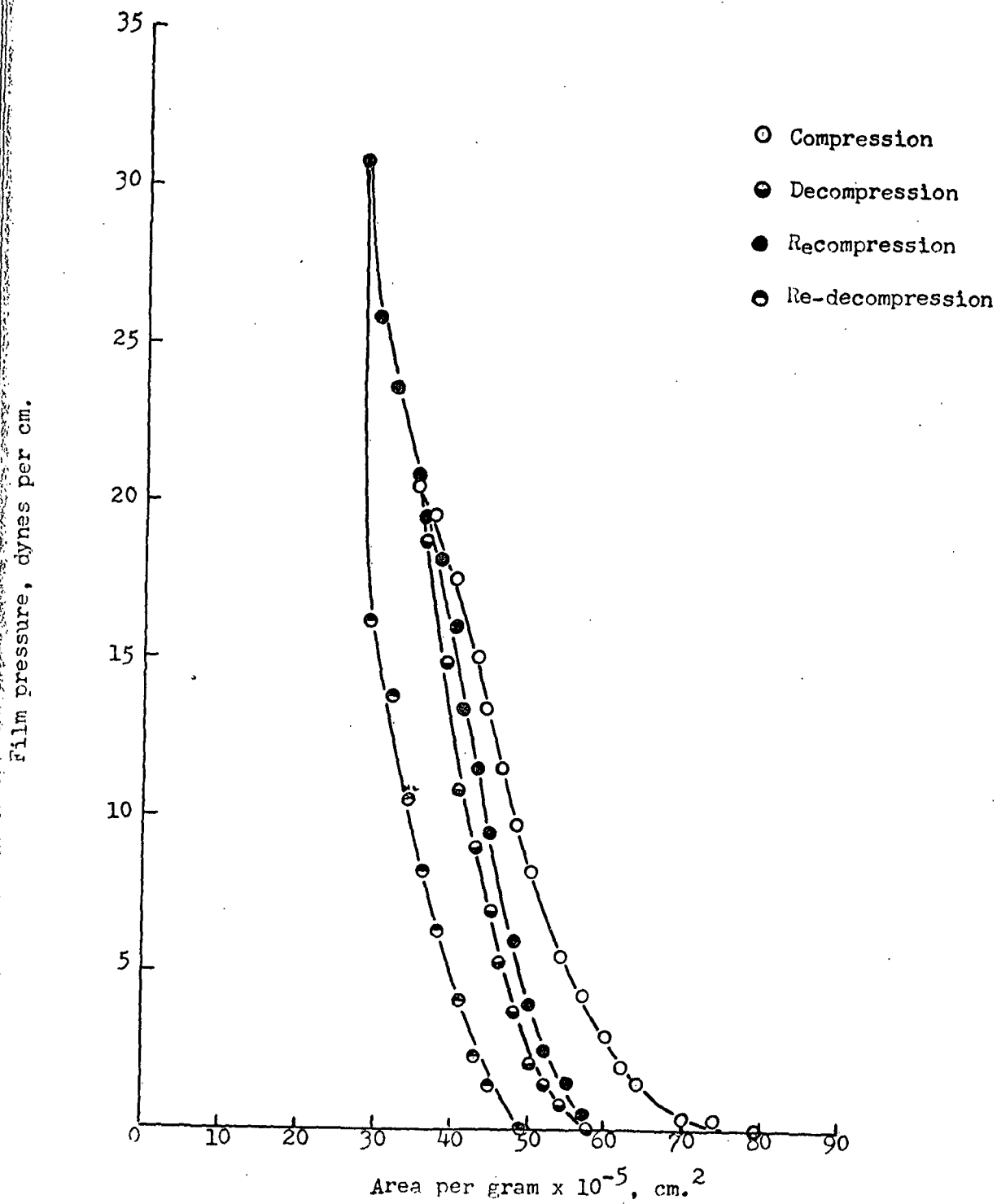


Figure 21

Film pressure-area curve for unsaponifiable fraction spread on tap water containing 8×10^{-6} M calgon. pH 8.1, Temperature 25°C .



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APPENDIX
Table VII

Film pressure-area data for stearic acid spread on dilute hydrochloric acid
pH 2.2, temperature 21°C.

Film pressure, dynes per cm.				Film area cm. ²	Area per molecule A ^{o2}
Compression	Decompression	Recompression	Re-decompression		
0				346	22.8
	0			339	22.4
			0	335	22.1
		0.79		329	21.7
	0.48			328	21.6
			0.79	325	21.5
49				323	21.3
	1.33			320	21.1
		2.22		317	21.0
			2.76	312	20.6
26	3.88	4.79		310-308	20.4
	5.42		5.26	302	19.9
		8.59		300	19.8
80				298	19.7
	7.80		7.45	296	19.5
		12.55		292	19.3
41	10.81			288	19.0
			11.89	285-284	18.8
	13.00	14.96		278	18.3
37				276	18.2
			14.42	273	18.0
	16.58			269	17.7
		19.37		266	17.6
			18.92	264	17.4
68				259	17.1
		28.18		253	16.7
				251	16.6

Table VIII

Film pressure-area data for whole pitch spread on dilute hydrochloric acid
pH 1.7, temperature 23°C.

Film pressure, dynes per cm.		Film area, cm. ²	area per gram x 10 ⁻⁵ , cm. ²
Compression	Decompression		
0		474	77
0		371	61
1.65		348	57
	0	339	55
2.06		329	54
2.76	0.89	314-310	51
4.18		297	48
	1.33	291	47
	1.71	273	44
7.10		265	43
	3.96	248	41
8.91		239	39
	5.77	230	38
9.67		225	37
10.30		215	35
	6.85	209	34
11.22		200	33
11.89	8.24	187-184	30
12.74		173	28
	9.92	164	27
14.26		147	24
15.37		125	20
16.26		111	18
	15.75	95	15
18.20		83	14
18.73		72	12
	17.97	67	11
19.84		63	10
20.54		54	9
21.90		42	7
22.92		35	6
24.60		27	4

Table IX

Film pressure-area data for fatty acid fraction spread on dilute hydrochloric acid. pH 2, temperature 23°C.

Compression	Film pressure, dynes per cm.			Film area, cm. ²	Area per gram x 10 ⁻⁵ , cm. ²
	Decompression	Recompression	Re-decompression		
59				416	99
78				397	94
0				367	87
35				353	84
			0	326	77
79				311	74
			0.29	298	71
18				296	70
			0.95	275	65
72				270	64
			1.14	262	62
43				255	60
89				243	58
31	8.81			234	56
	9.95		3.01	224	53
		10.94		221	52
44	11.60		4.79	212-211	50
		13.98		206	49
00			6.75	200-198	47
	14.80	16.61		196-195	46
46	17.63		8.97	187-186	44
		19.97		182	43
38				175	42
	21.56			173	41
			11.25	170	40
92		22.60		165-164	39
			12.58	160	38
			14.14	154	36
		23.52		148	35
		23.97		131	31
			22.63	125	30
		24.60	24.19	106-104	25
		25.14	24.66	90	21
		25.61		74	18
			25.36	72	17
			25.99	61	15
		26.66		56	13
		27.26		45	11
			27.17	44	10
		29.07		33	8

Table X

Film pressure-area data for resin acid fraction spread on dilute hydrochloric acid. pH 1.5, temperature 24°C.

Film pressure, dynes per cm.		Film area, cm. ²	Area per gram x 10 ⁻⁵ , cm. ²
Compression	Decompression		
3.33		468	71
3.68		456	69
4.50		440	67
5.33		421	64
6.66		399	60
	0	390	59
7.77		385	58
	0.22	375	57
9.89		355	54
	0.54	351	53
11.35	0.79	334-333	50
	1.43	317	48
13.16		312	47
	2.85	297	45
15.12	3.55	283	43
	4.56	269	41
15.47		268	40
	6.31	246	37
15.98	7.32	233-232	35
16.23		220	33
16.23	8.75	214-210	32
16.64	9.99	201-198	30
16.74		186	28
	11.98	170	26
17.53	12.84	157-147	24
17.91	13.41	147-143	22
18.35	14.33	131	20
19.05	14.90	114-113	17
19.97	15.56	99-97	15
	16.48	86	13
20.86		82	12
21.81		72	11
	17.37	68	10
22.48	18.16	63-58	9
23.36		55	8
24.95		44	7
25.74	22.79	35	5

Table XT

Film pressure-area data for unsaponifiable fraction spread on dilute hydrochloric acid. pH 2, temperature 21°C.

Film pressure, dynes per cm.		Film area, cm. ²	Area per gram x 10 ⁻⁵ , cm. ²
Compression	Decompression		
0		410	68
0.89		392	65
1.30		372	62
1.71		361	60
	0	307	51
7.39		302	50
	0.41	288	48
11.54	0.95	271	45
	1.90	262	44
13.79		257	43
	2.76	252	42
15.22		246	41
	4.12	243	40
16.20	5.71	237-233	39
17.66	8.18	225-221	37
	10.78	210	35
19.84		205	34
	13.57	200	33
22.73	15.72	189-184	31
	18.26	179	30
24.66		174	29
29.23		157	26

Table XTT

Film pressure-area data for whole pitch spread on distilled water.
pH 6.3, temperature 21.5°C.

Film pressure, dynes per cm.		Film area, cm. ²	Area per gram x 10 ⁻⁵ , cm. ²
Compression	Decompression		
0		474	77
0		448	73
0		422	69
0		397	65
0		371	61
0.44		346	56
1.01		326	53
1.39		310	51
	0	307	50
2.00		297	48
	1.7	288	47
2.30		280	46
	1.20	269	44
4.44		265	43
5.93	1.97	252	41
	3.39	237	39
7.07		236	38
8.18	5.20	221	36
9.35	6.78	204-202	33
10.49	8.24	187-184	30
11.57	9.51	172-169	28
12.68		155	25
13.63		142	23
	12.05	134	22
14.55		128	21
	13.41	122	20
15.60		115	19
16.48	14.61	105	17
	16.41	92	15
17.72		87	14
18.61	17.88	76-72	12
19.94	19.18	63-61	10
21.02		52	9
	20.26	51	8
22.35		41	7

Table XIII

Film pressure-area data for fatty acid fraction spread on distilled water. pH 6.5, temperature 21.5°C.

Film pressure, dynes per cm.				Film area, cm. ²	Area per gram $\times 10^{-5}$, cm. ²
Compression	Decompression	Recompression	Re-decompression		
.82				422	100
.08				406	96
.49				387	92
.81				370	88
.60	0			352	83
	0.57	0.63		335-333	79
.71				330	78
		1.27		323	76
.53				315	75
	1.17			312	74
		1.81		310	73
.20				302	72
	1.90			301	71
		2.47		297	70
.50	2.47	3.55	0	288-285	68
	3.46		0.44	275	65
.93				271	64
		5.10		266	63
	4.25			264	62
.51			1.39	259-257	61
	5.36	6.40		353	60
			2.03	148	59
0.97	6.18			246-243	58
		7.77		242	57
2.33			2.92	236-234	56
	7.29			233	55
		9.51		229	54
4.17	8.40		4.34	225-223	53
		11.41		218	52
			5.39	212	50
6.74	10.81	13.82		209-205	49
	12.36		6.88	198	47
9.56		15.85		196-195	46
			8.24	189	45
2.06		18.48		183-182	43
			9.32	177	42
		20.45		174	41
		23.01		164	39
		24.38		152	36
			21.75	137	32
		25.07		127	30
		25.36		116	28

Table XIV

Film pressure-area data for resin acid fraction spread on distilled water.
pH 6.5, temperature 21.5°C.

Compression	Film pressure, dynes per cm.			Film area, cm. ²	Area per gram x 10 ⁻⁵ , cm. ²
	Decompression	Recompression	Re-decompression		
				499	75
				474	72
				448	68
				422	64
				397	60
.48				372	56
.82				360	54
.17				346	52
.65				332	50
.03				320	48
.76				307	46
.36				296	45
.12				283	43
.39				262	40
.44	0	0.48		246-242	37
.73	0.48	1.27		234-230	35
		2.35		223	34
.56	1.46			219	33
		3.90	0	211-210	32
.67	2.25			207-206	31
.90		5.14		198-197	30
	3.71	6.28	0.2	195-189	29
1.86	5.33			186-183	28
		8.21		177	27
3.16	6.66		1.74	174-173	26
	8.15	9.76	2.73	165-163	25
.39		10.78		161-159	24
5.56	9.83	12.11	4.18	154-150	23
	11.98		5.20	143	22
6.64		13.57		140-138	21
	14.90	15.25	6.63	132-129	20
8.13				125	19
8.86	17.12	16.90	8.12	120-118	18
8.86		18.39	9.16	114-110	17
		19.05	11.10	101-100	15
		19.97	13.19	92-91	14
		21.24	15.41	79-77	12
		22.22	17.97	68-67	10
		23.33	19.81	59-58	9
		24.76		50	8
		25.36		42	6

Table XVI

Film pressure-area data for whole pitch spread on sodium hydroxide
substrate. pH 11.3, 24.5°C.

Film pressure, dynes per cm.				Film area, cm. ²	Area per gram $\times 10^{-5}$, cm. ²
Compression	Decompression	Recompression	Re-decompression		
0				448	73
0.29				422	69
0.29				397	65
0.29				371	61
0.29				346	56
0.79				314	51
1.62				298	49
2.31				288	47
3.23				276	45
3.96			0	266-262	43
5.33			0.54	253-251	41
6.34			1.93	241-237	39
7.93			2.92	227-225	37
8.97			4.09	214	35
9.70				201	33
			5.55	198	32
			7.07	188	31
11.10				184	30
			7.93	177	29
12.20			9.19	168-165	27
			10.21	157	26
13.28				156	25
14.14			11.57	145-142	24
15.15			12.14	133	22
16.48			12.90	119-118	19
17.75			13.98	106-105	17
19.02			15.28	97-96	16
20.19			16.80	87	14
21.56			18.48	78	13
	19.46			76	12
23.43		20.61	20.45	69-68	11
25.17		22.63		61-60	10
27.01	25.55	24.54	23.08	58-52	9
28.53			25.74	50-48	8
		27.67		45	7
29.80		30.43		38-36	6

Table XVII

Film pressure-area data for fatty acid fraction spread on sodium hydroxide substrate pH 10.0, temperature 23.5°C.

Compression	Film pressure, dynes per cm.		Re-decompression	Film area, cm. ²	Area per gram x 10 ⁻⁵ , cm. ²
	Decompression	Recompression			
1.30				440	104
1.30				406	96
1.17				329	78
1.17				317	75
1.17				289	69
1.17				266	63
1.17				242	57
1.17				224	53
1.17				198	47
1.17				184	44
1.33				148	35
1.52				128	30
	1.01			104	25
3.23				100	24
	1.01	1.01		97-96	23
			0.79	90	21
9.41	1.65	1.65		86-84	20
	4.50	4.09	1.78	73-70	17
13.41	8.24	10.11	5.42	60-58	14
19.27	14.80	16.96	12.14	47-45	11
24.22				40	9
27.58			25.04	33	8
		28.09		31	7

Table XVIII

Film pressure-area data for resin acid fraction spread on sodium hydroxide
substrate pH 11.0, temperature 25°C.

Film pressure, dynes per cm.				Film area, cm. ²	Area per gram x 10 ⁻⁵ , cm. ²
Compression	Decompression	Recompression	Re-decompression		
1.08				410	62
1.08				397	60
1.14				348	58
1.14				319	48
1.14				280	42
1.33				255	38
1.46				238	36
1.71				207	31
1.97				188	28
2.25				175	26
2.95	1.11			160-156	24
3.93		1.30	0.82	146-143	22
	1.39			140	21
5.52				132	20
		2.03	0.98	128	19
7.93	2.16			118	18
		3.49	1.49	114-113	17
9.92	3.80			108-106	16
		5.55		102	15
12.84			3.96	95-93	14
		9.54	6.53	88-86	13
16.86				78	12
	11.32	13.44	9.99	74-73	11
19.81				68	10
23.78	17.66	15.85	17.28	63-58	9
	23.62	23.84		52-50	8
28.59			24.73	46-45	7
	30.59	29.39		40-38	6
31.07		31.98		36-32	5

Table XIX

Film pressure-area data for unsaponifiable fraction spread on sodium hydroxide substrate. pH 11.0, temperature 25°C.

Pressure	Film pressure, dynes per cm.			Film area, cm. ²	Area per gram x 10 ⁻⁵ , cm. ²
	Decompression	Recompression	Re-decompression		
0				461	77
0				430	71
0				410	68
8				387	64
4				371	62
0				358	60
5				346	57
1				332	55
7				317	53
7				302	50
6				289	48
27				274	46
27			0	261	43
67			0.25	246-244	41
23			1.65	233	39
88	13.06		3.52	219-218	36
		14.46	5.86	212-211	35
30	13.76	17.76		207-202	34
79	15.82		9.38	201-196	33
		20.03	12.05	193	32
73	17.91	21.87		187-186	31
			14.90	183	30
12	19.97	24.47		174	29
			18.20	169	28
		28.85		164	27
92	25.99		22.63	159-156	26
71		34.87		152-150	25
				145	24

Table XV

Film pressure-area data for whole pitch spread on a distilled water
substrate containing 5×10^{-4} M aluminum ion. pH 4.1, temperature 24°C .

Film pressure, dynes per cm.		Film area, cm. ²	Area per gram $\times 10^{-5}$, cm. ²
Compression	Decompression		
0		448	73
0.16		422	69
0.16		384	63
1.24		366	60
2.16	0	352-348	57
3.33		338	55
	0.51	332	54
4.56	1.17	321-317	52
5.74	1.74	307-305	50
6.85		293	48
	2.38	289	47
8.12	3.14	276-275	45
	3.90	264	44
8.91		261	43
9.51	4.76	250-248	41
	5.58	237	39
11.16		229	37
11.70	6.94	218	35
12.43		206	34
	7.80	205	33
13.03		193	32
	8.53	192	31
13.63		182	30
14.23		169	28
	10.27	166	27
15.18		156	25
	11.32	148	24
16.26		142	23
	12.08	136	22
17.47		129	21
18.45	12.90	119-118	19
19.53		105	17
	14.90	99	16
20.54		95	15
21.56	15.75	84-83	14
22.67	17.47	70-69	11
23.30		60	10
	19.65	54	9
24.12		51	8
	21.59	45	7
25.99		37	6
26.28		32	5

Table XXI

Film pressure-area data for fatty acid fraction spread on distilled
 water substrate containing $5 \times 10^{-4} M$ aluminum ion. pH 4.1
 temperature $24^{\circ}C$.

Compression	Film pressure, dynes per cm.		Re-decompression	Film area, cm. ²	Area per gram $\times 10^{-5}$, cm. ²
	Decompression	Recompression			
				435	103
				397	94
				352	83
0.76				306	72
1.19	0			289	69
		0.73	0	284-283	67
	1.08			278	66
0.99				274	65
		2.79	0.38	271-269	64
	2.03			266	63
0.71				262	62
		4.25	1.52	259-257	61
	3.65			253	60
0.96				250	59
		6.72	2.47	246-244	58
	5.42			241	57
0.62			4.18	236	56
		9.83		230	55
	7.80			229	54
			5.71	225	53
0.90		12.90		218	52
			7.77	216	51
	11.57			212	50
0.54		16.01	9.70	205	49
	14.23			202	48
0.24			11.89	195-193	46
		20.73		192	45
			13.66	184	44
0.58				182	43
		26.82		177	42
			16.55	172	41
		27.42		166	39
			19.27	161	38
		28.05		157	37
		25.99		150	35

Table XXII

Film pressure-area data for resin acid fraction spread on a distilled water substrate containing 5×10^{-4} M aluminum ion. pH 4.1 temperature 24 C.

Compression	Film pressure, dynes per cm.		Re-decompression	Film area, cm. ²	Area per gram x 10 ⁻⁵ , cm. ²
	Decompression	Recompression			
59				443	67
55				429	65
38				412	62
18				399	60
	0.70		0	393-388	59
61	1.33			385-383	58
29	1.81	3.42		374-369	56
.84			1.08	365-362	55
		5.48		357	54
.84	3.14		2.03	352-351	53
		7.29		346	52
.30	4.62		3.27	339-338	51
		9.73		332	50
6.61	5.96	11.92	4.91	328-321	49
	7.13			320	48
		13.85	6.47	314-311	47
0.03	9.22			306	46
			8.81	301	45
4.22				291	44
	11.82		11.22	285-284	43
3.37	12.68	17.66		278-275	42
			12.39	274	41
		22.22		262	40
3.13	14.20		13.63	261-260	39
	16.67	25.87	15.98	253-250	38
		30.62		242	37
5.06				239	36
	21.62	33.73		230	35
		37.34	28.75	217	33

Table XXIII

Film pressure-area data for unsaponifiable fraction spread on distilled
 water substrate containing 5×10^{-4} M aluminum ion. pH 4.2
 temperature 21.5°C.

Compression	Film pressure, dynes per cm.			Film area, cm. ²	Area per gram $\times 10^{-5}$ cm.
	Decompression	Recompression	Re-decompression		
0.76				431	72
1.17				411	68
1.78				399	66
2.47				387	64
3.52	0.29			374-371	62
	0.60	0.63		369-365	61
4.50	1.11	1.59		357-355	59
5.58	2.47	3.01		344-340	57
6.75		4.72		332	55
	3.55			328	54
7.96	4.98	6.50	0.29	320-317	53
9.29			0.67	310-308	51
10.65	6.82	8.72		303-298	50
	8.15		1.81	297-296	49
12.33		11.00	2.85	289-287	48
	11.06			282	47
13.76		13.63	3.49	278-275	46
	13.25		4.56	271-269	45
14.71				268	44
15.50		14.65	5.83	261-257	43
		16.04	7.70	250-246	41
		17.09		241	40
			9.83	236	39
		18.70		229	38
			12.30	223	37
		20.00		216	36
			13.50	211	35
		21.05		206	34
		22.63	15.06	198-196	33
		24.69	17.28	188-184	31
			21.14	174	29
		26.85		172	28

Table XXIV

Film pressure-area data for whole pitch spread on tap water containing
 8×10^{-6} M calgon. pH 8.1, temperature 25°C .

Film pressure, dynes per cm.		Film area, cm. ²	Area per gram $\times 10^{-5}$, cm. ²
Compression	Decompression		
0		461	75
0		435	71
0		410	67
0.41		371	61
0.67		355	58
1.20		339	55
2.03		326	53
2.60	0	314-310	51
3.65		298	49
4.69		285	47
	0.79	284	46
	2.85	256	42
9.03		250	41
	4.88	233	38
9.89		224	37
	7.20	218	35
10.81		211	34
	8.72	200	33
11.57		198	32
	9.51	189	31
12.74		186	30
13.85		172	28
	11.98	164	27
15.06	12.93	156-154	25
16.14	14.17	143-140	23
16.99		133	22
18.32		120	20
19.88	17.59	106-105	17
21.49	19.34	95-90	15
22.92		84	14
	21.68	77	13
24.88	23.39	70-65	11
27.26		58	9
	26.18	51	8
29.48		45	7
30.50		36	6

Table XXV

Film pressure-area data for fatty acid fraction spread on tap water
containing 8×10^{-6} M calgon pH 8.7, temperature 24.5°C .

Film pressure, dynes per cm.				Film area, cm. ²	Area per gram $\times 10^{-5}$, cm.
Compression	Decompression	Recompression	Re-decompression		
0				461	109
0.57				422	100
0.95				407	96
1.43				372	88
2.38				338	80
3.01				317	75
3.77				301	71
	0			294	70
4.79				287	68
5.52		0.70		274-273	65
	0.63			262	62
		1.11		259	61
7.29				253	60
	1.24	1.87		247	59
8.62	2.06			238-234	56
		2.85		233	55
10.24	2.92			225-224	53
		4.22	0	221-218	52
11.54				212	50
	4.09		0.54	207-205	49
		5.99		202	48
13.35				200	47
	5.29			195	46
15.15				189	45
		8.12	1.52	187	44
	6.72			182	43
			2.47	177	42
18.04		10.52		174	41
	8.56			169	40
		12.68	3.71	164-163	39
	10.97			160	38
21.52				156	37
		15.56	5.07	152-151	36
	13.16			148	35
24.50			6.37	143-142	34
	15.18	18.64		140-138	33
27.20				132	31
	17.75	22.67		128-127	30
			9.83	124	29
			12.11	116	28
		27.14		113	27
			13.79	105	25
		29.42		101	24
			17.91	95	22
		31.10		87	21
			23.24	84	20
		31.10		64	15

Table XXVI

Film pressure-area data for resin acid fraction spread on tap water containing 8×10^{-6} M calgon. pH 7.4, temperature 25°C.

Compression	Film pressure, dynes per cm.			Film area, cm. ²	Area per gram $\times 10^{-5}$, cm. ²
	Decompression	Recompression	Re-decompression		
0.79				443	67
0.79				421	64
0.79				320	48
1.08				294	44
1.49				282	43
1.90				265	40
2.60				248	38
3.14				238	36
3.90				223	34
4.50	0			210-209	32
	0.29	0.79		198-196	30
5.86				193	29
6.66	0.73			186-183	28
		1.39		182	27
7.96	1.20		0	174-172	26
	1.90	2.60		168-164	25
		4.18		159	24
9.76	3.14		0.51	154-151	23
		5.29		149	22
11.29	4.91			142-141	21
13.00	6.59	7.99	1.68	136-132	20
14.77	8.31			123	19
		10.37	4.72	122-120	18
16.58	10.71	13.28		113-110	17
18.61			7.13	108-104	16
20.48	13.38	16.48		100-97	15
22.57	17.91	20.92	13.28	88-83	13
24.98				78	12
		24.09	16.80	76-73	11
	22.25	26.85	19.65	65-64	10
28.24				61	9
29.67		29.48		51-50	8
	26.06		23.78	49-47	7
31.70		31.70		42	6
32.27		33.60		36-35	5

Table XXVII

Film pressure-area data for unsaponifiable fraction spread on tap water containing 8×10^{-6} M calgon pH 8.1, temperature 25°C.

Film pressure, dynes per cm.				Film area, cm. ²	Area per gram $\times 10^{-5}$, cm. ²
Compression	Decompression	Recompression	Re-decompression		
0				474	79
0.32				448	74
0.38				422	70
1.55				388	64
2.16				374	62
3.04				360	60
	0			352	58
4.31		0.54		342-340	57
		1.46		329	55
5.45	0.82			326-325	54
	1.43	2.54		315	52
8.24	2.19	3.90		303	50
			0	294	49
9.76	3.77	5.96		291	48
11.57	5.33			279	46
	6.97	9.51	1.39	273-269	45
13.50				268	44
15.12	8.94	11.54	2.31	260-259	43
	10.81	13.44	4.15	250-246	41
17.59		15.98		241-239	40
	14.80			237	39
		18.13	6.34	230-229	38
19.46				221	37
	18.77	19.59	8.21	218	36
20.45		20.83		210-209	35
			10.59	206	34
		23.62	13.85	192	32
		25.87		182	30
			16.29	173	29
		30.81		166	28