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THE BEHAVIOR OF THIXOTROPIC FLUIDS

IN CONSTANT SHEAR RATE EXPERIMENTS

by

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in Candidacy for the Degree of
Master of Science
in
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LIST OF SYMBOLS

F = shear stress, dynes/cm^2

F_p = initial value of shear stress (at time = 0)

F_{ss} = steady state value of shear stress (at time equal infinity)

$F'' = (F - F_{ss})/(F_p - F_{ss})$

$F' = (F - F_{ss})/F_{ss}$

D = shear rate, seconds^{-1}

t = time, seconds

u = viscosity, poise or gram/(cm - sec)

k = constant from data reduction (intercept), subscripted 0,1,or 2 for each exponent

m = constant from data reduction (slope), seconds^{-1} subscripted as "k"

K = structure level constant for power law region

n = power law constant

I. ABSTRACT

The lack of an adequate quantitative theory of
thixotropic behavior is due to an incomplete understanding
of the phenomena. When sheared at a constant rate a
thixotropic fluid shows a decreasing shear stress as a
function of time. These transient stress curves were
analyzed in terms of an exponential series by the Tobolsky-
Murakami procedure. This analysis was successful with a
number of different thixotropic fluids. The three
exponential terms represent three distinct mechanisms,
each with its own particular time constant. The time
constants were found to be functions of the present shear
rate and the previous history of the fluid. These
functions defied quantitative description.

Curves of constant structure were generated from
buildup behavior under shear. These curves followed the
power law at the higher shear rates. A method is given
whereby any curve of constant structure may be computed
for the power law region of a particular fluid. It is
recommended that future work be directed toward this
area, i.e. definition and study of structure grids in
the fluid. When structural levels are known, the changes
and mechanisms of change in these levels can be more
fruitfully studied.

II. INTRODUCTION

When subjected to a constant shear rate a thixotropic fluid shows a decreasing apparent viscosity (shear stress) with time. A brief survey of previous work in this field will show that thixotropy is an incompletely understood phenomenon. Yet fluids that exhibit thixotropic behavior are widespread. Foodstuffs, polymer solutions, clay suspensions, paints, biological and natural fluids are just a few examples. Consequently the study of thixotropic behavior has practical as well as academic importance.

The term "thixotropic" was originally employed by Freundlich (1)[*] to describe materials which undergo an isothermal gel- sol- gel transformation upon agitation and subsequent rest. The origin of the word "thixotropy" is from the Greek, "thixis" meaning stirring or shaking and "trepo" meaning turning or changing. The original definition has itself undergone changes. Thixotropy is currently defined in terms of the following characteristics, 1) completely reversible and isothermal nature, 2) structure change brought about by application of mechanical disturbance, e.g. shearing or shaking, 3) recovery of original structure when the disturbance is removed, and 4) a flow curve (F vs. D) showing the hysteresis effect. The fourth characteristic is really a consequence of the second and third.

Early attempts to analyze thixotropic behavior were centered on the hysteresis loop (14,29,33). Hysteresis loops can be obtained in many ways, but the usual method is to apply a slowly varying shear rate to a sample initially at rest. The resulting shear stresses are recorded as a function of shear rate. The shear rate is generally programmed as some continuous

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[*] This reference is an outstanding historical review and discussion of scientific investigation in this field.

and symmetric function of time, e.g. sine wave, triangular wave, etc. (11,14,24,25,29,33).

Other work has attempted to describe thixotropic behavior through the use of mechanistic arguments concerning entanglement and disentanglement of fluid units under stress. More recent work involves the use of continuum mechanics (6,7,8), chemical kinetics (10,18,21,23), and viscoelastic analogies (5). These theories have had varying degrees of success. However, there is still no adequate phenomenological theory to account for thixotropic behavior. The main reason for this is a lack of explicit knowledge of what is happening in the fluid and how changes in viscosity or "structure" are caused by outside influences. The concomitant problem is the formulation of these causes and effects into meaningful and predictive mathematics.

Ideally a general theory of thixotropic behavior would describe a) a shear thinning steady state flow curve with or without a yield value, b) the presence and size of thixotropic flow curves (hysteresis loops), c) shear stress decrease with time at constant shear rate after a step transition from a lower shear rate (breakdown curve), and d) shear stress increase as a function of time at constant shear rate after a step transition from a higher shear rate (buildup curves). If (d) is not measurable in the experimental time span, the theory should be adaptable to rest time experiments. In these experiments the peak shear stress (a measure of the gel structure) at one shear rate is found as a function of the resting time at zero shear (4). The form of the equations should be related to the mechanism(s) of structural change in the fluid. Any constants or unspecified functions must be easily determined from experimental data. The equations should be simple enough to be useful for fluid flow problems. These are major challenges to research and progress in

this field. The mechanism(s) for structural change are largely unknown. Structure and its rate of change have only recently been investigated (6,18).

One of the major difficulties in describing thixotropic behavior is the experiment. The design of proper experiments and the execution of these experiments are crucial to understanding the results. Experimental difficulties include subjecting the fluid to shear for very long periods of time, sample evaporation, maintaining constant temperature, machine inertia effects, limited shear rate range and measurable torque output, instrument electronics heating and response, and viscous heating of the sample. These problems have been minimized by methods described in the Experimental section of this report. A Couette viscometer with an electronic recording device and constant temperature attachment was used to record data of the following kinds,

a) breakdown curves at different shear rates on a sample that had rested for 19 hours.

b) breakdown curves at different rates of shear on a sample that had been sheared at a lower shear rate immediately preceeding.

c) buildup curves at various shear rates from "steady" stress values at immediately preceeding higher shear rates.

d) thixotropic loop generation.

e) repeat of experiments with different thixotropic fluids as a comparison.

The experimental goal of this research was to find a means of analyzing curves of stress vs. time at constant shear rate (Fig. 1), in order to gain an understanding of the mechanisms of thixotropic change. By varying the shear rate the effects of previous history and present shear could be studied.

Figure 1
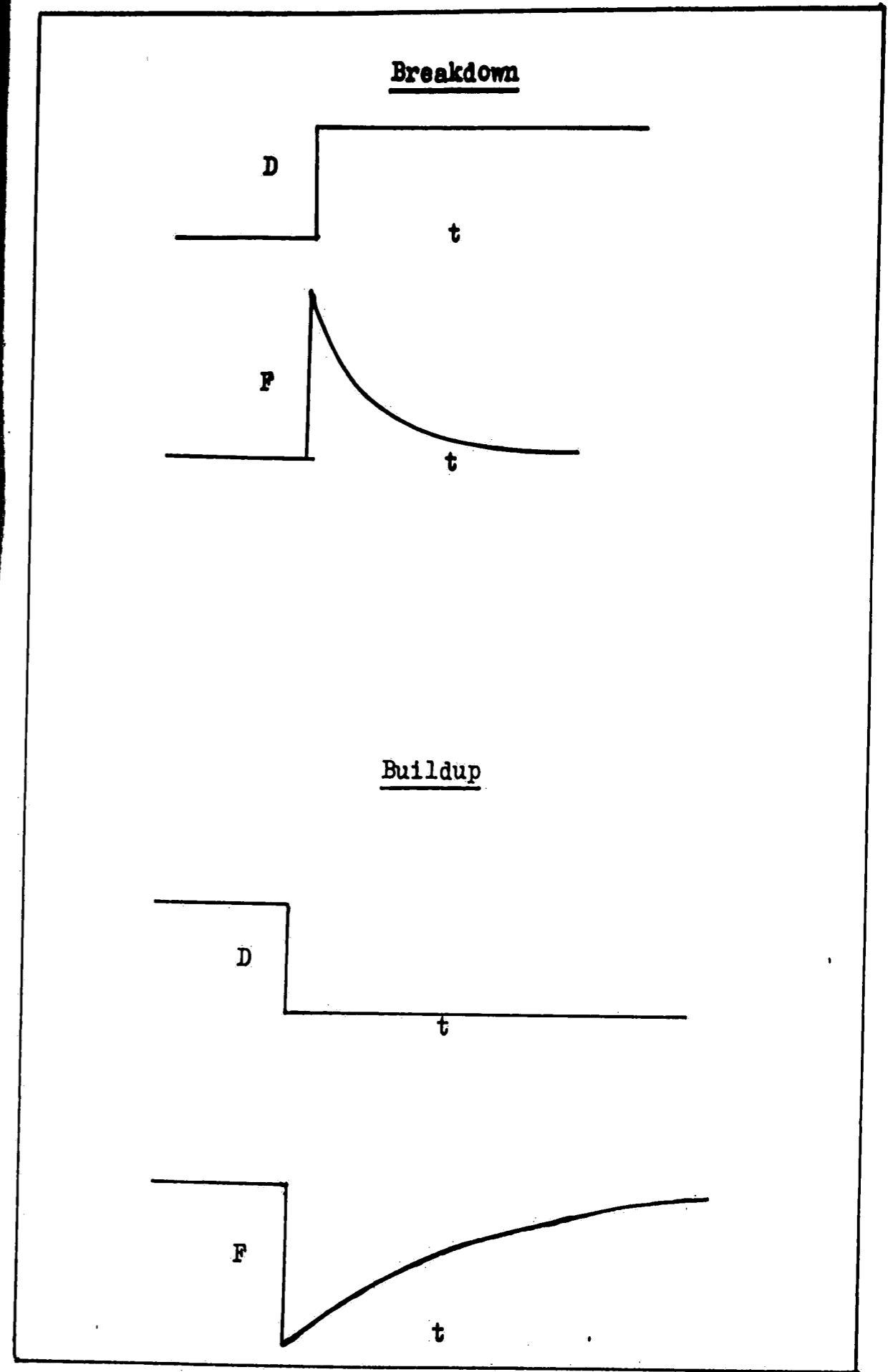
Breakdown

Buildup

The method of data reduction used in this work is applied to thixotropic breakdown and buildup for the first time. Previously Tobolsky's "Procedure X" had been used only in viscoelastic measurements (16,26,32). When applied to the stress vs. time curves, this method yields some new information and insights concerning the nature of the thixotropic phenomenon.

The main thrust of this work is to show that a variety of mechanisms are at work in thixotropic change. The exact nature of these mechanisms is still unknown, but the results of this work shed some light on their behavior and interrelationships. The definition and investigation of structural levels in a thixotropic fluid appear to be more readily available properties. Thus future investigation should be directed to the concepts of structure and structure changes and not to the more directly evident concepts of time dependent viscosity.

III. DEVELOPMENT OF THE CONCEPTS OF THIXOTROPY

Historically the discovery and study of thixotropy began in the 1920's. The phenomenon which led to the concept of thixotropy was first reported in 1923 by Sohalek and Szegvari, who studied iron oxide dispersions in water.(1). The iron oxide gels had the property of becoming completely liquid through shaking alone, to such an extent that the liquified "gel" was hardly distinguishable from the original "sol". The sols reverted to the original gel state when allowed to rest for a period of time. The changes in state could be repeated a number of times without any visible change in the system. Peterfi (1927), who was working with cell plasm, noted that living cell content, originally "quite stiff", assumed a fluid consistency when agitated. After a passage of time the cell content returned to its original state. Based on the suggestion of Peterfi, Freundlich introduced the term "thixotropy" to science in a report on aluminum hydroxide gels (1). Within a short time the phenomenon of thixotropy was discovered in many systems. The early investigators found that a characteristic time of resolidification could be measured when agitation of the sol was stopped. Data from a Couette apparatus also demonstrated that the degree of liquifaction from the gel depended on the applied shear rate.

Research in this area expanded greatly in the 1930's. Investigators debated proper definitions and devised ways to characterize the newly discovered phenomenon. McMillen in 1932 made the observation that for thixotropic materials flow curves determined by succesively increasing the shear stress would not coincide with similar curves obtained at succesively decreasing shear stress. He was the first to show the importance of previous shear history

on thixotropic materials. Pryce- Jones in the late thirties demonstrated the existence of thixotropic properties in a wide variety of materials, e.g. creams, starch pastes, adhesives, emulsions, gelatin and paints, and illustrated qualitative differences in properties by the use of specially designed tests. Pryce- Jones favored controlling the speed of rotation (shear rate) in a Couette instrument and observing the changes in stress. The importance of time of shearing and rate of shear as factors affecting the viscous resistance to flow in thixotropic materials was clearly demonstrated. A general theory of thixotropic behavior was introduced in 1938 by Goodeve (12). The theory itself did not prove useful, but the concept of dynamic equilibrium did. In this situation a steady state is set up in the fluid under steady shear. This is a consequence of the shear and thermal breaking rates of so- called "links" in the system and of the shear and thermal making rates of these links. This formulation could account for the effects of such structural factors as Brownian motion, orientation, energy of activation of repulsive forces, collision rates, particle shapes and other dispersion micro- properties. These ideas were later expanded by Eyring and Brodkey. Green and Weltmann (1940's), the last of the "early" investigators, recommended and employed the use of thixo- tropic hysteresis loops to characterize the behavior of various systems (33,1,4). The use of these loops to compare different thixotropic systems found many adherents. Weltmann also applied the empirical curve fit approach to the transient shear stress curves at constant shear rate - without much success. The concepts of loop analysis are discussed extensively in references (1,11,19, 24,25,27,33).

Most of the recent work in thixotropy (since 1945) has been done in the last decade. In 1959 Eyring introduced

a theory of thixotropic behavior based on a mechanism
for fluid unit interaction with reaction kinetics con-
cepts. He assumed that two kinds of fluid units existed
in a thixotropic flow system, extended entangled units
which are non- Newtonian in character, and coiled dis-
entangled units which are Newtonian in character. He
also assumed that a reaction mechanism related the units
in a reversible transformation of entangled to disentangled
units. The relative amounts of the two types of fluid
units in a thixotropic system were determined by the
equilibrium constant for the above transformation. The
shear induced transition from entangled units to dis-
entangled units destroyed the structure in the material
and hence changed the initial solid- like nature to a
liquid. When the deforming force was decreased or removed,
the reverse transformation of disentangled to entangled
units was promoted and the material became more solid-like
in nature. A discussion of the mathematics can be found
in references (4,14,29). Eyring's theory was unique in
that it proposed a mechanism for changes in the fluid
while using the concept of a dynamic equilibrium between
rates of buildup and rates of breakdown. The Eyring theory
seems to give good agreement with reported experimental
results (14,29), and Billington has used aspects of the
Eyring theory to interpret his data (2,3). Eyring's
theory however, is not easily applied. The constants are
many, somewhat meaningless, and not easily obtained from
simple experiments.

Brodkey has expanded the rate concepts of Eyring
into a general interpretation of thixotropic behavior
and non- Newtonian flow.(10,18,21,23). The form of his
general relationship is a kinetics type rate equation
with empirically determined constants. The equation relates
the time rate of change of a normalized viscosity function

to the foward rate of reaction (breakdown) and the
reverse rate (buildup).

Cheng has developed to a degree a theory that
incorporates both non- Newtonian behavior and elements
of the rate theory (6,7,8). He states that the descrip-
tion of thixotropic behavior can be reduced to two
general relationships. The first is an equation of state,

$$F = u(\lambda, D)D$$

which relates the shear stress, F, to the shear rate, D,
through the viscosity, u. The viscosity is a function
of D and λ , the "structure" parameter. The second
equation is a rate equation,

$$\frac{d\lambda}{dt} = g_D(\lambda, D)$$

which describes the time rate of change in structure as
some function of the shear rate and the structure. The
forms of the functions are as yet unknown.

Jones and Brodkey have also studied the problem
of structure (18). It appears that future investigations
into thixotropic phenomena will be most fruitfully
studied in terms of structural levels and the shear induced
transitions from one level to another. This concept should
lead to a clearer understanding of the mechanisms and
nature of thixotropic change.

By this point it should be clear that previous
investigators have directed their efforts along many
different lines. Vinogradov has developed a theory based
on viscoelastic analogies (5) which is interesting, but
limited and weakly supported. Thermodynamic and energy
considerations have been developed by Kluitenberg (22)
and Järse (17). In a magnificently obtuse article
Kluitenberg shows there is very little to be gained by
that particular approach.

The empiricism of Weltmann and others is so far the
most useful and simplest way to characterize thixotropic

behavior. However, it is of little help in understanding
the phenomenon, since the thixotropic loop is no more
than an effect of many causes. The present work attempts
to separate and follow as many causes and effects as
possible. Analysis of literature data and repeat experiments
on different fluids were undertaken to show that the
results of this work are characteristic of thixotropic
behavior and not just of one particular fluid. Constant
shear experiments were chosen, because the causal factor
(shear rate) could be held constant while the changes in
effect (shear stress) were recorded. Changing the
experimental procedure allowed exploration into other areas
of the phenomenon, notably the effect of previous shear
history.

IV. EXPERIMENTAL PROCEDURE

When a thixotropic fluid is subjected to a constant
shear rate, the viscosity decreases with time (Fig.2,
breakdown curves). After a long period of constant shearing,
the viscosity will reach a steady value. This value of
viscosity or shear stress is the characteristic steady
state value for that particular shear rate. This value
can be approached from above or below depending upon the
previous history (Fig. 3). If the previous shear rate was
higher than the present shear rate, the approach will be
from below, i.e. the initial viscosity will be lower than
the steady state value. Highly thixotropic fluids, such
as Clay 4, will exhibit spontaneous buildup of shear stress
under a constant shear rate. If the previous shear rate
was lower than the present shear rate, the initial viscosity
will be higher than the steady state value. The closer
the previous shear rate to the present shear rate, the
smaller the difference between the initial viscosity and
the steady state value. This is true for both the break-
down and the buildup phenomena.

The apparent viscosity is defined as the shear stress
divided by the shear rate,

$$u = F/D.$$

The data are plotted in terms of shear stress for convenience.
Curves in terms of viscosity will show the same type of
time dependent behavior so long as the shear rate remains
constant.

The steady state flow curve of a thixotropic fluid
usually shows a yield value and shear thinning behavior
(Fig. 4). The rate of change in shear stress with respect
to shear rate is due to both a thixotropic structure change
and to the non- Newtonian nature of the fluid. As will
be shown later, the steady state flow curve passes through
a number of structural states (6,18). The apparent viscosity

Figure 2

breakdown

F, dynes/cm^2

⊙ - previous shear @ 0 sec^{-1}
× - previous shear @ 16 sec^{-1}
⊡ - previous shear @ 48 sec^{-1}

t, seconds

buildup

F, dynes/cm^2

⊗ - previous shear @ 420 sec^{-1}
▽ - previous shear @ 1260 sec^{-1}

t, seconds
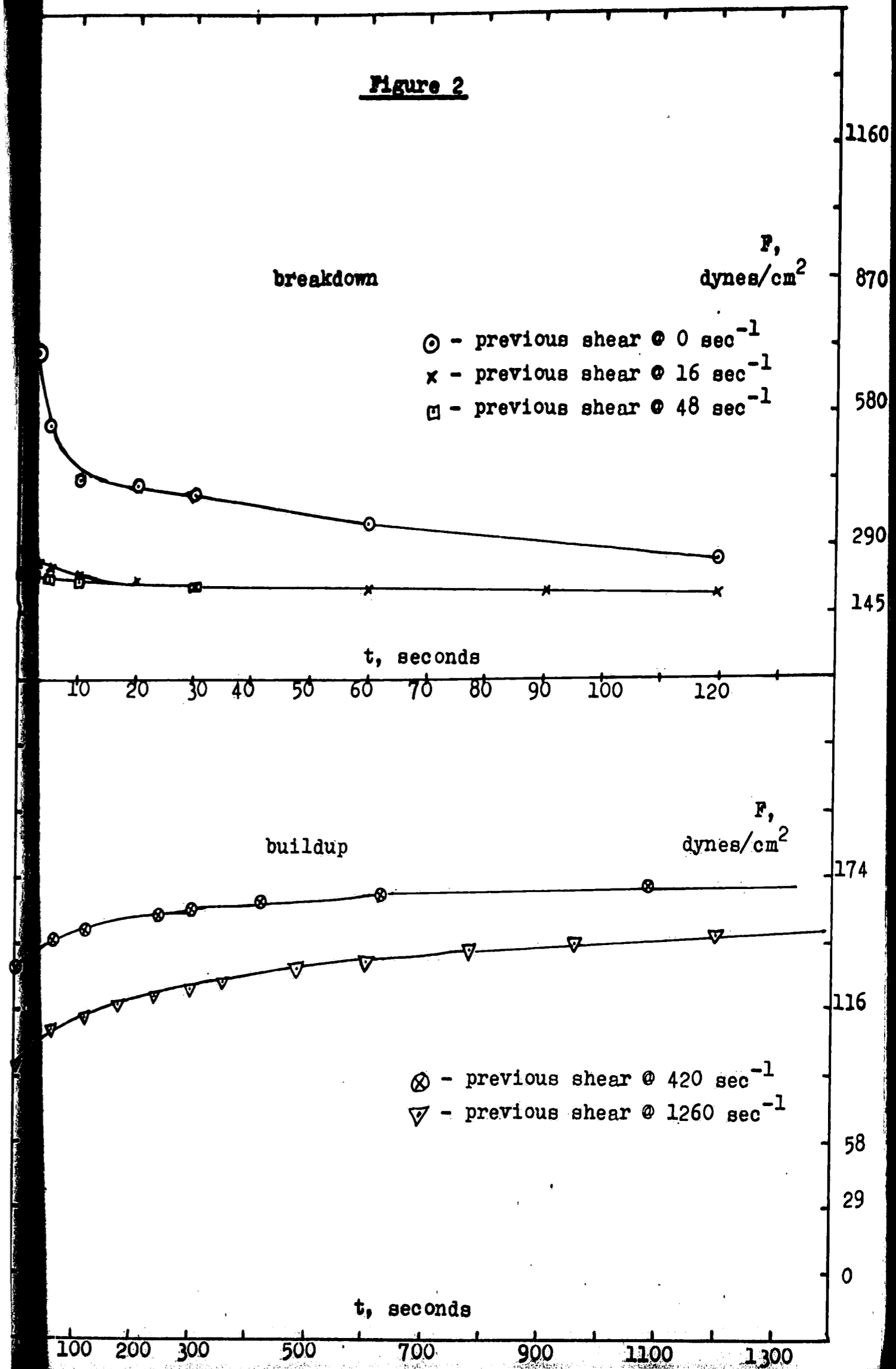
Figure 3

⊙ — rest history breakdown
at 70 sec^{-1}

x — buildup at 70 sec^{-1} from
previous ss @ 420 sec^{-1}

$1/t$,
sec^{-1}

F, dynes/cm^2
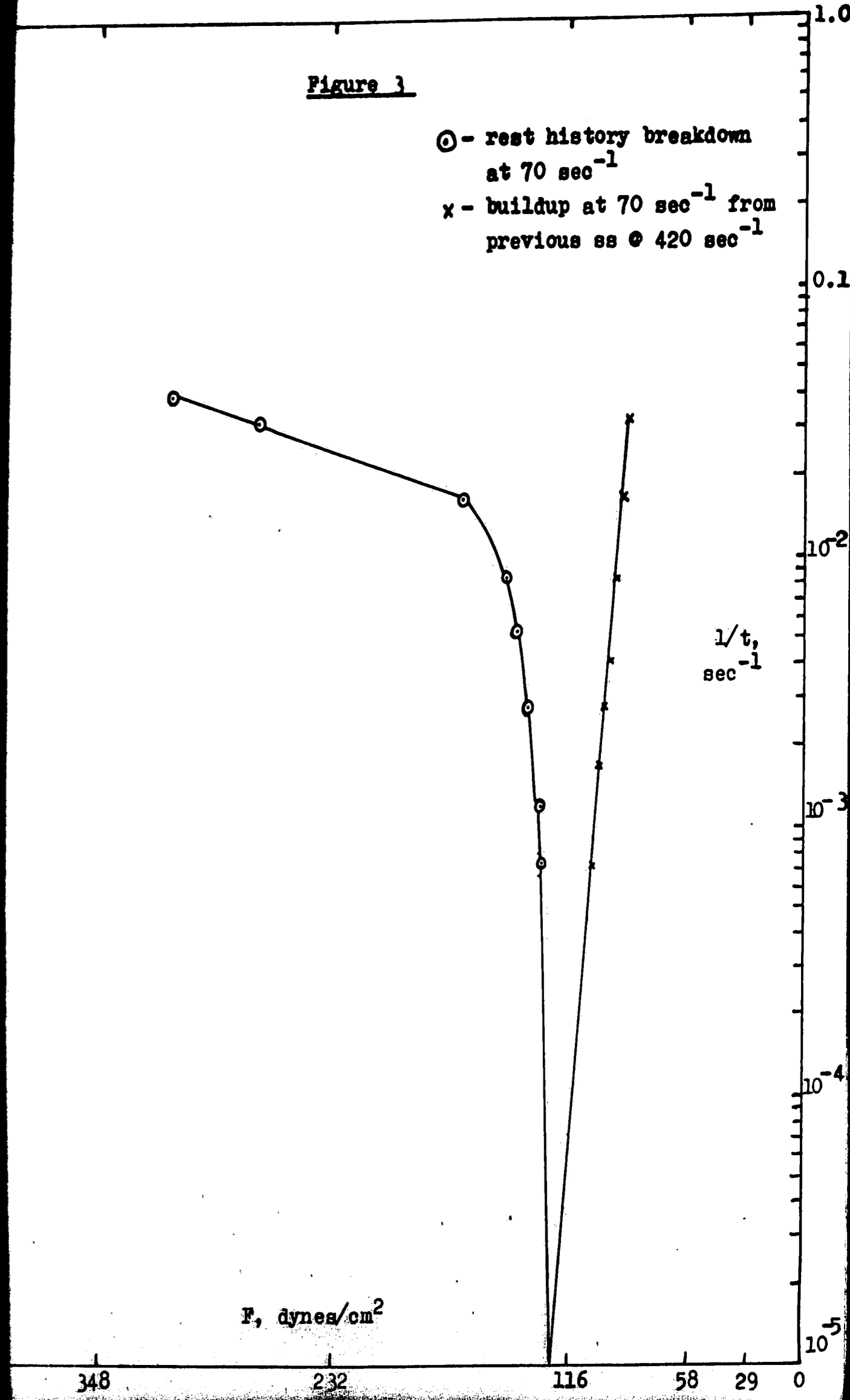
vs. shear rate plot shows a characteristic shear thinning nature (Fig. 5).

The resistance to flow, as measured by the existing shear stress, is used as an indication of the structural state of the fluid for these transient experiments. The elusive quantity called "structure" is defined by the shear stress. Structural levels or curves of constant structure are obtained by equating the final stress values at one shear rate with the initial values at another. In this work structure defined by a steady value of shear stress at a higher shear rate is equated with that of an initial value of shear stress at an immediately following lower shear rate. The time expended in changing from one shear rate to the other is negligible relative to any time required for changes in the fluid. By using different shear rates a curve of constant structure can be obtained (see Results and Discussion section).

The following experiments were designed and the data recorded (see Appendix for equipment and materials specifications). The breakdown and buildup curves were generated by choosing a reference shear rate (one of the ten available of the Rotovisco viscometer). The fluid was placed in the machine, sheared at the highest rate for two minutes, and then allowed to rest overnight for 19 hours to regain its gel structure (within about 95%). The fluid was then subjected to the reference shear rate, and the rest history breakdown curve was recorded continuously as a function of time. The fluid was immediately thereafter subjected to the lowest available shear rate and allowed to build up its structure for approximately twenty minutes (or until a reasonably steady value of shear stress had been attained). A switch to the reference shear rate was then accomplished, and the resulting breakdown curve for that previous history was recorded.

Figure 4

Steady State Flow Curve for Clay 4
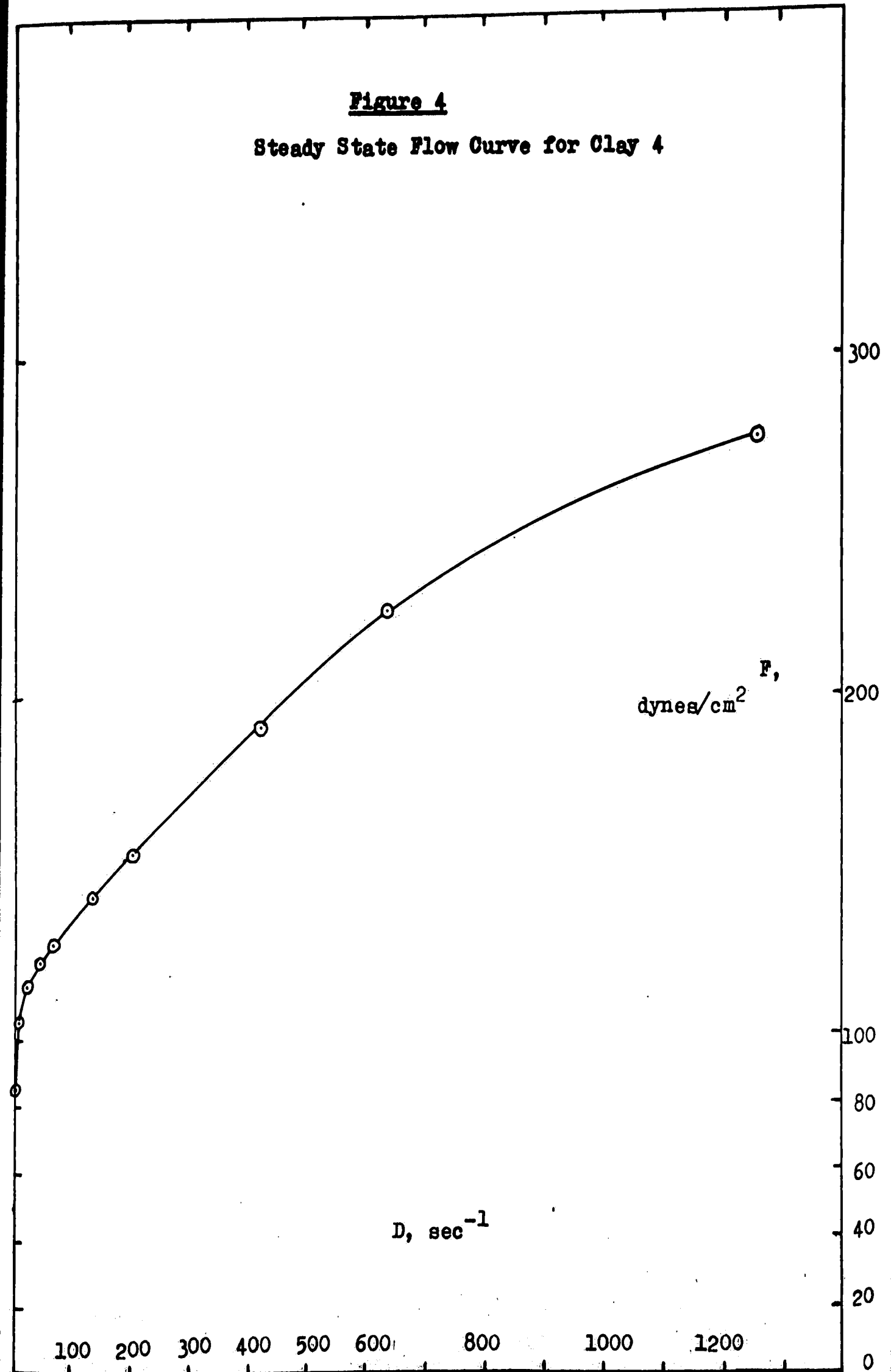
Figure 5
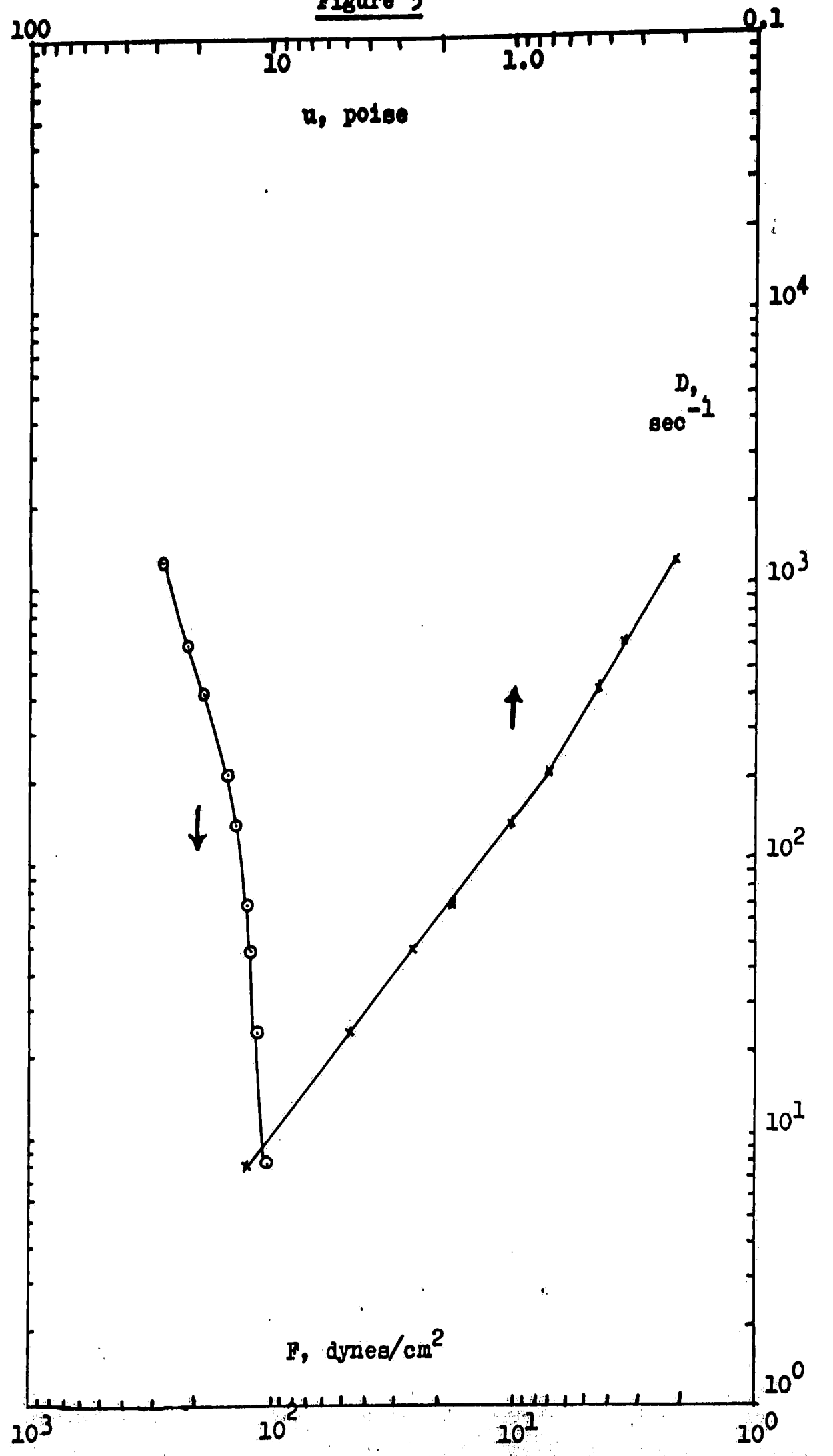
After the steady value of stress had been reached to within about 5%, the shear rate was switched to the next lowest shear rate and the buildup recorded. This process was repeated until the highest shear rate was reached. By switching from shear rates lower than the reference shear rate to the reference shear rate, breakdown curves of varying previous history were generated. Similarly, when changing from a higher shear rate to the reference shear rate, buildup curves at the reference shear rate were generated with different previous histories. Changing from the reference shear rate to lower shear rates gave a family of buildup curves at different shear rates with the same previous history. Varying the reference shear rate from day to day gave a complete picture of the fluid's behavior over the available rates of shear. Ideally, a complete flow curve and constant structure curves could be generated from these experiments. However, it is almost impossible to wait for the fluid to reach steady state when structure is building up, because the time required for such buildup is infinite. Thus curves of constant structure determined from final values of stress in buildup curves could not be constructed with any accuracy.

Other thixotropic fluids were subjected to a spot test of one reference shear rate experiment to check their behavior. Mayonnaise, a thixotropic paint, 1.0% and 1.5% (by weight) carboxy- methylcellulose solutions in water were tested in addition to the clay. These fluids were also subjected to a loop test for comparison. It was not possible to generate the usual slowly varying flow loop, since the shear rate could not be programmed. Rapidly changing the shear rate by shifting through the gears, as one goes through the gears of a Porsche, could not be done without getting very large inertia effects in the upcurve. The loops were generated by first shearing at the

lowest available shear rate to a steady value of shear stress. To complete the upcurve the shear rates were increased in step fashion (each to a quasi- steady stress value) to the top shear rate. The downcurve was obtained with virtually constant structure by rapidly decreasing the shear rate in step increments. Three seconds were allowed for each reading on the downcurve portion, and the total time ranged between 25 and 30 seconds. For fluids whose buildup response was slow or negligible in this time period constant structure was maintained.

Other experiments were carried out for additional information and for a check on the conditions of the experiment. Inertia effects were measured by placing water in the Couette assembly and subjecting it to a series of step changes in shear rate. The torque output was recorded continuously as a function of time. Inertia effects were present as manifested by an inertia "peak" which lasted for about three seconds for the higher shear rates (see Fig. 29). The degree of inertia effects present with other more viscous fluids was undetermined. The temperature was maintained at $20^\circ C$ by a constant temperature bath assembly. Viscous heating was checked by Poehlein's analysis (28) and by generalized correlation supplied by the instrument company in the operating manual (13). The operating conditions were free from viscous heating effects (see Appendix).

Most thixotropic fluids exhibit a yield value, a stress below which no flow occurs. This yield value is due to the gel structure of the fluid. Once the gel is broken by shearing the fluid no longer has this yield point. To measure this yield value or characteristic gel strength a reducing gear was used, and the procedure of Heinz (15) was followed. The fluid was subjected to a very low shear rate ($0.08 \ sec^{-1}$) until a steady stress value was recorded

for about two minutes. The shear was removed and the final stress recorded. This "residual" stress was the yield value. These are reported along with the loop data (Table V).

A number of techniques were required to surmount or minimize the difficulties involved in experimentation. Constant temperature was maintained, and viscous heating problems were found to be non- existent. However, when the instrument is running constantly from four to six hours, the electronics heat up. To avoid large changes in response wet towels were placed over the machine housing. This served to prevent gross overheating and minimized changes in the instrument's sensitivity. Care had to be taken in choosing the fluids, so that the torque readings did not go off scale. In the case of Mayonnaise a different sensing head was used to record the very high stresses. The shear rate range was the same for all experiments to facilitate comparison and for simplicity. The biggest experimental headache was sample evaporation, both during testing and when resting over- night. Wet towels were wrapped around the Couette assembly to keep the relative humidity at 100%. Polyethylene film was wrapped around the towels to cut water loss. This method seemed to work, but care had to be taken not to have the towels too wet, as much of the vapor would con- dense on the inside of the cup and change the properties of the fluid by dilution.

A final experiment was tried more out of curiosity than anything else, but the results were startling. After breakdown at top shear the fluid was subjected to the reference shear rate and allowed to build up. After 20 to 30 minutes of buildup under shear the instrument was turned off, and the fluid was allowed to rest for 20 minutes. It was assumed that in this period of time the

fluid would continue to build up, perhaps even as far
as the steady value at the reference shear rate. After
20 minutes the fluid was again subjected to the reference
shear rate and the time response continuously recorded.
The result was a breakdown curve whose peak was above
the steady state stress value. The final value (after
five to ten minutes) was identical to the value of stress
attained by the previous buildup curve, _viz_. below the
steady stress value at the reference shear rate (see Fig.
30). This behavior occurred in Clay 4 at every reference
shear rate used. The experiment was not tried for the
other fluids, because their buildup characteristics
were not nearly as strong as Clay 4.

V. SUMMARY OF RESULTS AND DISCUSSION

This section has been divided into the following categories for convenience and clarity, 1) a discussion of the breakdown curves for Clay 4, 2) analysis of breakdown curves of other thixotropic fluids, 3) a discussion of the buildup curves for Clay 4, 4) a discussion of hysteresis loop experiments, 5) a discussion of constant structure curves, and 6) a discussion of other experimental data, e.g. yield value and inertia data.

A word should be said about the choice of axes in plotting the data. The stress vs. time curves were clearly non-linear, and they were not analyzable in terms of simple functions. The stress was not an exponential function of time, nor was it linear when plotted against log t, $t^{\frac{1}{2}}$, or t^2. The stress was then normalized and plotted on a logarithmic scale against linear time. At large times straight line behavior appeared. The choice for the normalizing function was straightfoward: Division by either the initial or final stress value did not work very well. However, when the final value was subtracted from the stress value at any time and the result divided by either the final value or the difference between the initial and final values, a reasonable function was obtained. The function F" approached zero as time approached infinity and the stress approached the steady value. The function F", $((F - F_{ss})/(F_p - F_{ss}))$, was used in plotting the breakdown curves, in order to constrict the curves as much as possible. All curves then started at 1.0 and approached the same steady value at a particular shear rate. None of the curves coincided, as it was hoped they would. The same function was used with the buildup curves yielding similar results. When the initial value, F_p, was removed from the normalized function, the effects of

previous history could be clearly followed. The curves
for the same shear rate did not all start at 1.0, since
the stress at time zero was different in each case. The
normalized function F', $((F - F_{ss})/ F_{ss})$, was used in
plotting the buildup curves, where the previous history
was more accurately interpretable.

The experiments on Clay 4 took about two weeks to
perform, and the clay remained in the apparatus from day
to day. The data for the earlier portion of the experi-
ment were fairly consistent, but those for the later
portion were inaccurate due to evaporation losses from
the sample. Unused fluid had to be stored carefully,
since the clay changed its properties when stored in a
sealed jar for a long period. To avoid this problem, a
dessicator jar was used to store the fluid. Water was
placed in the bottom, so that 100% relative humidity was
maintained. Reasonably consistent data are presented
for six shear rates for the Clay 4 breakdown and buildup
studies (Table I).

The transient curves were interpreted as a series
of exponentially decreasing terms. Procedure X was used
to reduce the data to these terms. A material must show
simple exponential behavior at long times for this method
to work. The data did show linear behavior at long times
when plotted as log F'' or log F' vs. time. To get the
short time characteristics the long time contribution
was subtracted from the original curve, and the resulting
points were replotted as $\log(F'' - k_2 \exp(-m_2 t))$ vs. time.
Graphically this is represented by replotting the differences
between the original curve and the straight line fit to
the long time behavior. If the second plot is a curve,
the procedure is repeated until the data are reduced to
straight lines. The final analysis yielded a sum of
three exponential terms for these experiments, i.e.

TABLE I

Maximum buildup of stress, S in millivolts.
$F = 29\,S$, in dynes/cm^2

previous shear, sec^{-1}	1260	630	420	210	70	8
present shear, sec^{-1}						
1260	--	9.8	9.5	--	9.5	9.6
630	7.0	--	7.8	7.6	7.6	7.4
420	5.9	6.9	--	6.6	6.8	6.8
210	4.4	5.3	5.2	--	5.3	--
140	--	4.5	4.5	--	--	5.0
70	3.1	3.7	3.7	3.7	--	4.4
48	--	--	3.3	3.3	--	4.2
24	2.3	2.8	2.8	2.9	3.7	4.0
16	--	--	--	--	3.6	--
8	2.3	2.6	2.5	2.6	3.4	--

$$F'' = k_0 \exp(-m_0 t) + k_1 \exp(-m_1 t) + k_2 \exp(-m_2 t).$$

Breakdown Curves

The results of these experiments reveal some interesting and frustrating trends. Table II shows that neither the slopes (m) nor the intercepts (k) seem to follow any simple relationship with respect to shear rate or previous history. The long time behavior constants, k_2 and m_2, appear to be almost independent of shear rate, but in view of the rest of the data this conclusion seems to have little meaning. The three exponential terms seem to do an excellent job in fitting the data. The fit can be thought of as the result of a discrete spectrum of characteristic times. Each time constant, m_i^{-1}, is sufficiently different from the other two, such that each can be said to govern a particular area of the time response. Evidence for the above conclusion is based on the fact that the curves do exhibit a marked linear behavior at large times. Consequently the long time behavior is governed by a single time constant.

The so- called time constants can be interpreted in mechanistic terms as follows: The early period (1 - 10 seconds) can be described as the fluid's initial response to the sudden imposition of shear. The structure is suddenly torn apart in gross chunks. With time the fluid's response changes to less dramatic breakdown and tearing apart of structure, because there are no large chunks of structure to rend asunder, as it were. This period is governed by the intermediate time constant. The final response (from about 100 seconds to the steady state) can be described in terms of a slow grinding or such like, where the structural elements are made more uniform. At the steady state the final form of the structure would be

TABLE II

Rest history breakdown curves at different shear rates
Data reduction constants

shear rate sec^{-1}	"k", dimensionless			"m", sec^{-1}		
	k_0	k_1	k_2	m_0	m_1	m_2
1260	.841	.082	.077	0.49946	0.02473	0.00209
630	.916	.064	.020	0.34440	0.02468	0.00173
420	.903	.074	.023	0.29172	0.03920	0.00244
210	.861	.120	.019	0.26400	0.04834	0.00226
70	.557	.420	.023	0.64685	0.05493	0.00209
8	.690	.190	.120	1.18000	0.05454	0.00176

characteristic for the fluid at that particular shear rate. The time constants appear to be complicated functions of both the shear rate and the previous history. This behavior defies quantitative description.

Interpretation of the early portion of the curves was hindered by undetermined inertia effects, especially at the high shear rates where most of the reliable data were taken. Experimental accuracy, sensitivity, and experience are necessary to get breakdown curves that inspire confidence. Figures 6 and 7 are indicative of the type of behavior exhibited by Clay 4 for a breakdown curve experiment. History effects are not well defined, because a steady stress value was not reached at the previous shear rate. Previous shear history manifests itself in smaller peak heights (initial stress values) and stresses closer to the steady state. This is expected behavior, since the fluid with previous shear history already has less structure than the fluid from the gel state. Data reduction of breakdown curves with different previous histories yielded the three term exponential series fit. Changes in the time constants were not analyzed because of the uncertain structure level at the previous shear rate. Curves for varying histories at other shear rates are given in the Appendix (Data).

Figure 6

⊙ - original data
✕ - first reduction
⊡ - second reduction
D= 1260 sec^{-1},
rest history

Figure 7

$\odot$ - previous shear @ 420 sec^{-1}
$\triangle$ - previous shear @ 70 sec^{-1}
$\square$ - previous shear @ 8 sec^{-1}
$\times$ - first reduction of $\square$
$\ominus$ - second reduction of $\square$
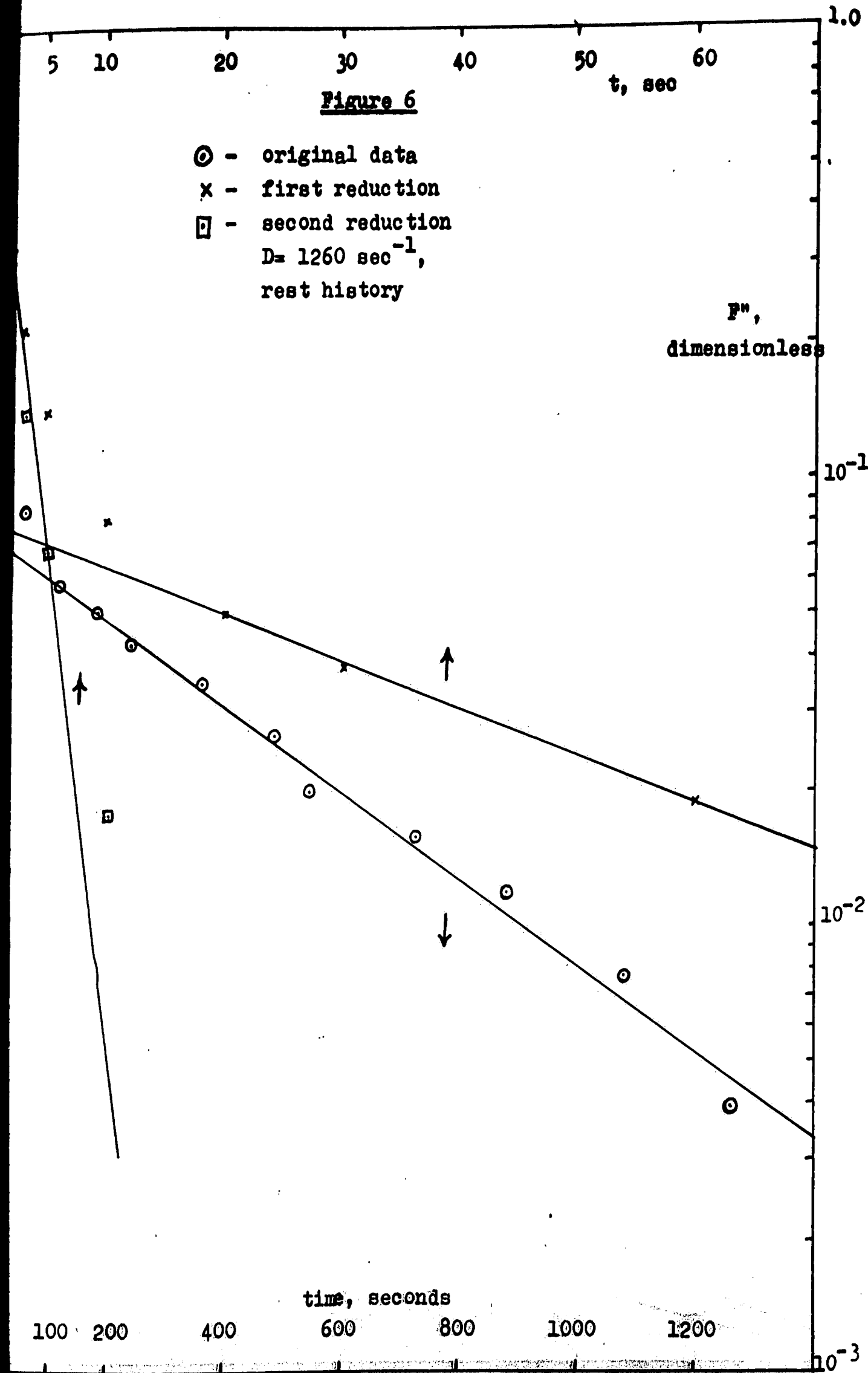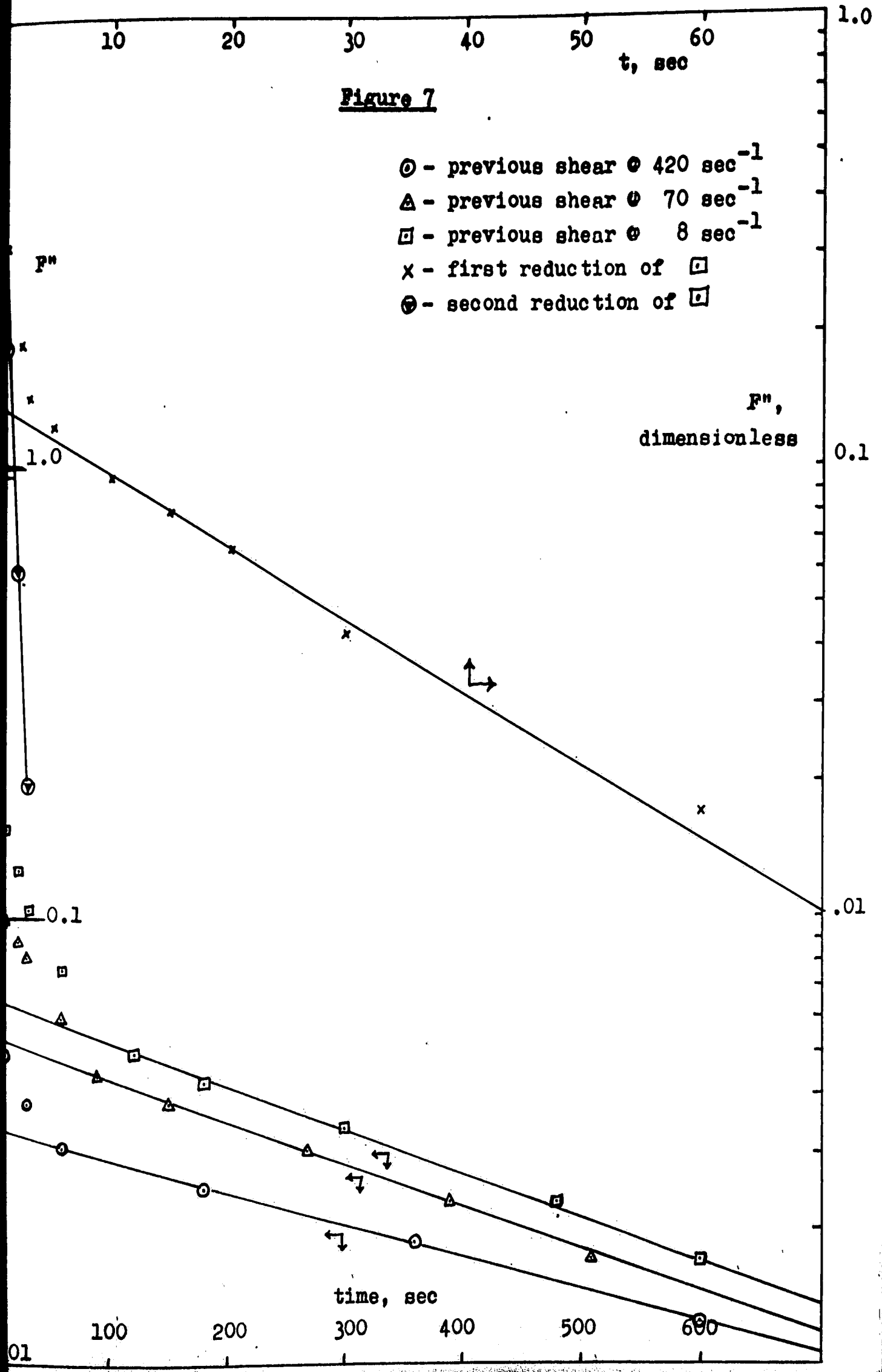
Analysis Applied to Other Fluids and Literature Data

There was some question at this point whether
the analysis chosen was valid for all thixotropic fluids.
It was shown for one fluid, that the analytical procedure
yielded three terms in all cases. Different shear rates
and previous histories changed only the values for the
constants.

Other known thixotropic systems were subjected to
a standard test to check their behavior. Most of these
fluids exhibited negligible buildup under shear, hence
only the breakdown curves are reported. The fluids were
a thixotropic paint, mayonnaise, 1.0% and 1.5% cmc- water
solutions. Breakdown data at constant shear rate from
the literature were scarce, but two good sources were
found (2,4). Eyring's data (14) could not be transferred
with sufficient accuracy and was not considered.

The results were encouraging. Procedure X worked
exactly as it had before, given the idiosyncrasies of
the data, e.g. a two term fit to one of Casey's curves
was due to incomplete reporting of the time response.
Three time constants were found to be characteristic,
and the long time behavior was again a straight line
indicative of a single first order mechanism. A two term
fit was sufficient for the 1.0% cmc- water solution.
This fluid flowed readily when inverted and did not have
the strong gel network of the other fluids. The interpretation
of these curves relative to each other, i.e. to the
classification of different fluids, is deferred until the
section discussing the loop behavior of these fluids.
The data are illustrated in Table III and Figures 8- 15,
inclusive.

TABLE III

Data reduction summary for other thixotropic fluids

fluid	shear rate sec^{-1}	"k", unitless				"m", sec^{-1}	
		k_0	k_1	k_2	m_0	m_1	m_2
1	140	.43	.57	---	.10226	.01347	.----
2	140	.36	.24	.40	.11776	.01082	.00231
3	140	.32	.40	.28	.22287	.02310	.00393
4	140	.29	.48	.23	.16831	.02076	.00169
5	2.8	.39	.46	.15	.65680	.06506	.00522
6	50.7	.63	.27	---	.47027	.02089	.----
7	unspecified	.42	.40	.18	.08283	.00595	.00055
8	"	.28	.42	.30	.04391	.00865	.00061

Note: Fluid (1) is 1.0% cmc- water, fluid (2) is 1.5% cmc- water, fluid (3) is mayonnaise, fluid (4) is a thixotropic paint, fluid (5) is Casey's fluid from (4) page 46, fluid (6) is Casey's fluid from (4) page 47, fluid (7) is Billington's fluid A (2), and fluid (8) is Billington's fluid Bl (2).

Figure 8

1.0% cmc

⊙ - original data
x - first reduction
    rest history,
    D= 140 sec⁻¹

Figure 9

1.5% cmc

⊙ - original data
x - first reduction
⊡ - second reduction
    rest history,
    D= 140 sec^{-1}

Figure 10

Mayonnaise

⊙ - original data
x - first reduction
☐ - second reduction
    rest history, D= 140 sec^{-1}

Figure 11

paint

⊙ - original data
✗ - first reduction
▣ - second reduction
rest history,
$D = 140 \ sec^{-1}$

Figure 12

Casey's data

⊙ - original data
x - first reduction
▣ - second reduction
   $D = 2.81 \text{ sec}^{-1}$

Figure 13

Casey's data

⊙ - original data

✗ - first reduction

D= 50.7 sec^{-1}

F"

1.0

0.1

.01

time, seconds

10 20 30 40 50 60 70 80 90 100 120

.5 1.0 2 3 4 5 6 t, min 1.0

Figure 14

Billington's data, fluid A

⊙ - original data
x - first reduction
⊡ - second reduction

F"   F"

0.1

.01

0.1

time, minutes

10   20   30   40   50   60

Figure 15

Billington's data, fluid B1

⊙ - original data
x - first reduction
▣ - second reduction
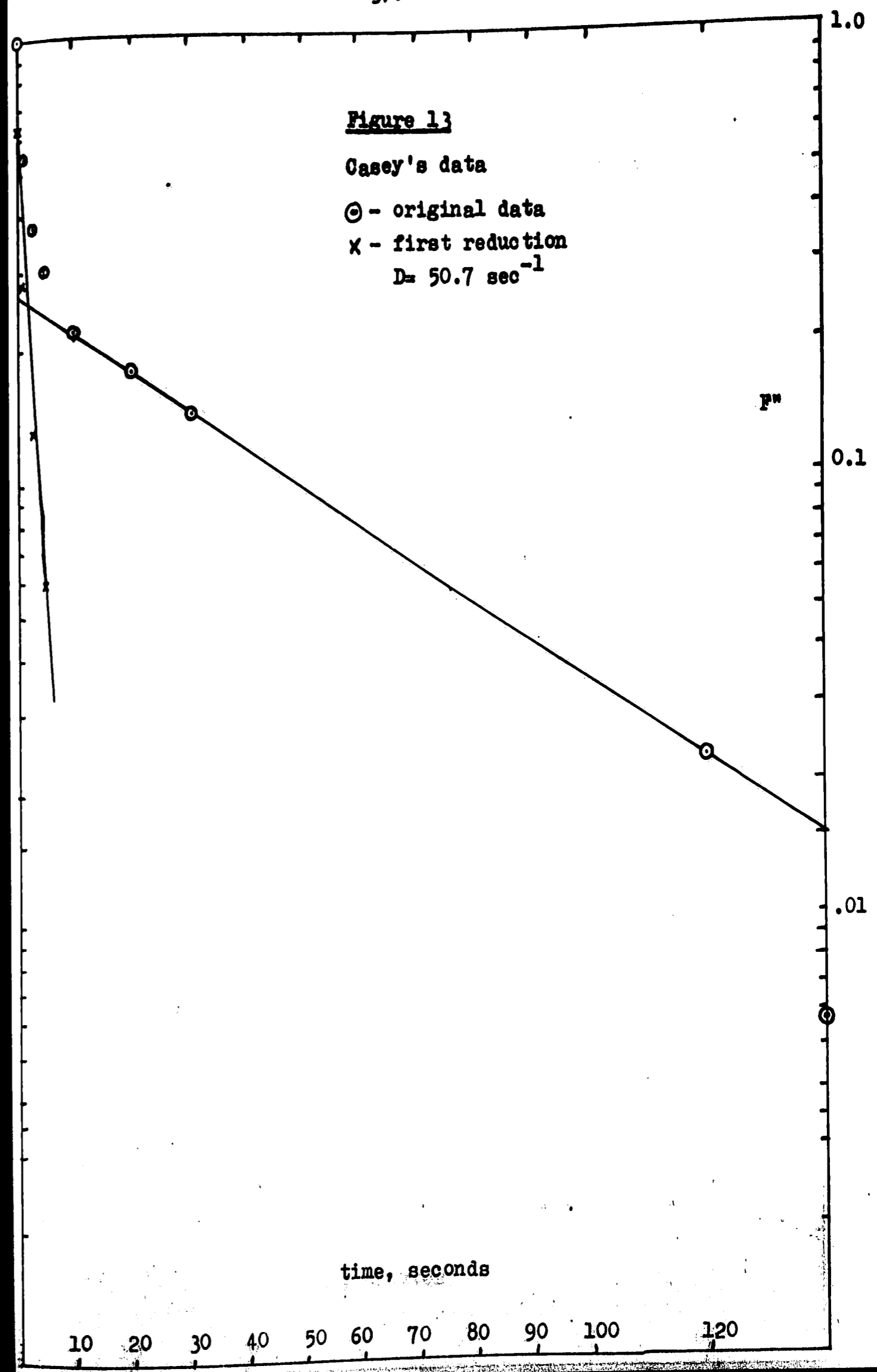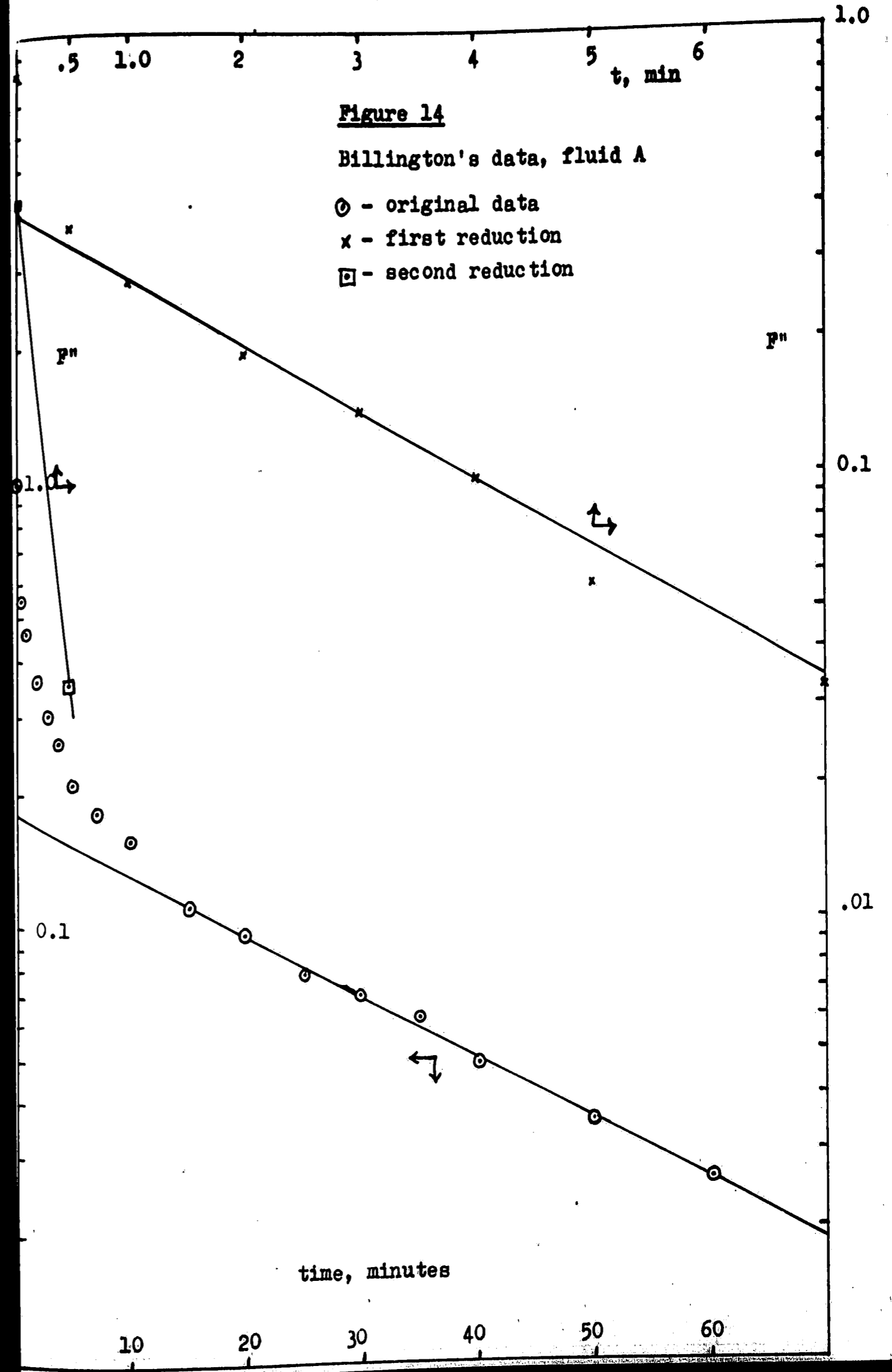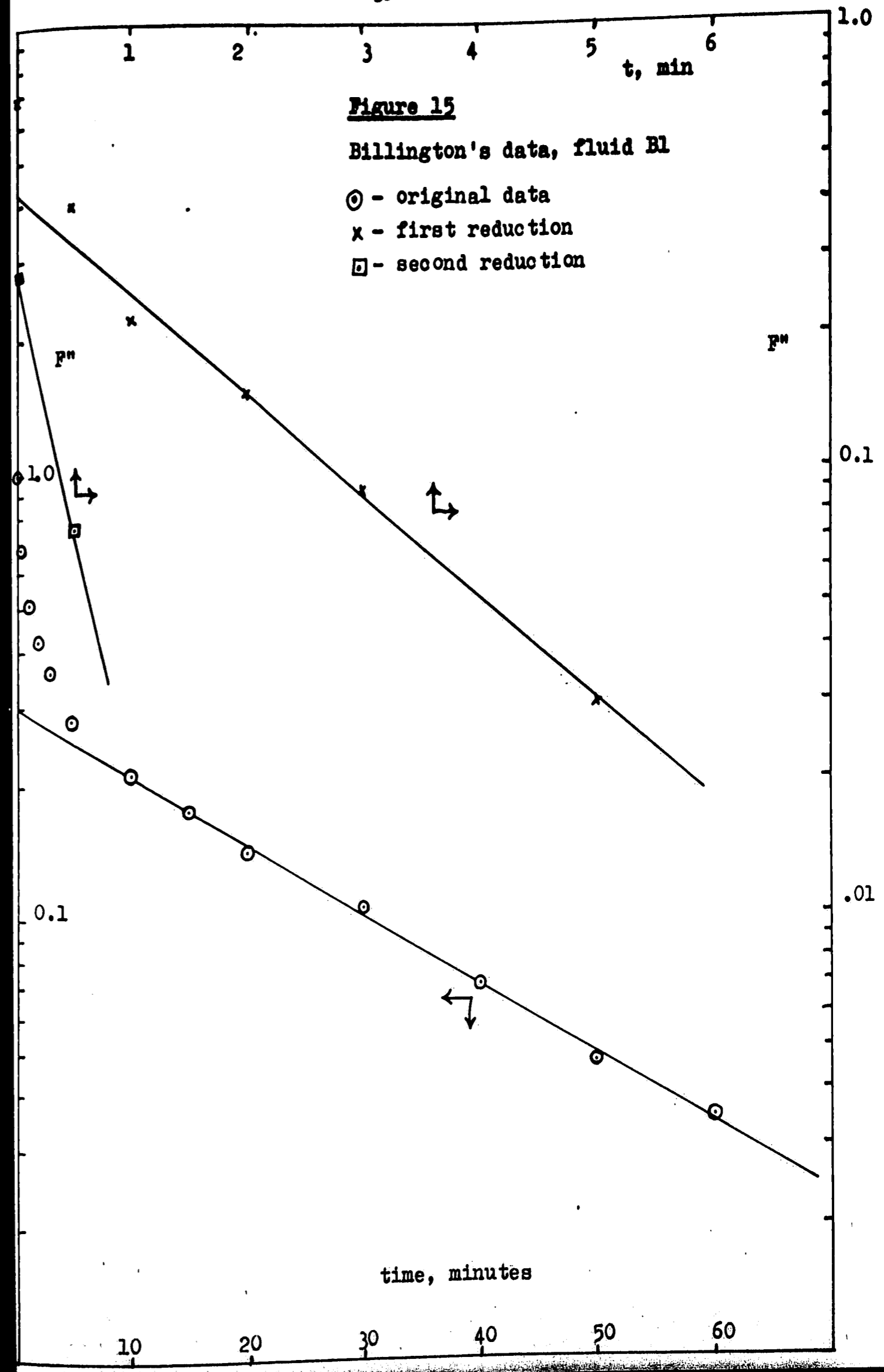
Buildup Curves

Not all thixotropic fluids exhibit measurable
buildup under shear in a reasonable amount of time.
A buildup curve is obtained for such fluids by measuring
the gel strength (peak shear stress values) at one shear
rate as a function of rest time (4). Clay 4 was the only
fluid tested to exhibit marked buildup characteristics
under steady shear.

Previous history and shear rate affect the buildup
curves as well. Analysis of buildup at different shear
rates with the same previous history was not very fruitful.
These data can be found in the Appendix. Analysis of
previous history effects at the lowest shear rate did
prove stimulating. The normalized shear stress in terms
of F', $(F- F_{ss})/F_{ss}$, was far more useful than F" in
revealing the effects of previous history. The changes
in initial values could be clearly followed.

Figures 16- 19 inclusive are indicative of buildup
under shear. These figures show that the lower the
previous structural level the longer the time required for
steady state. The increase in slope (at long times) as
a function of decreasing previous structure is shown
clearly on the graphs. The slope is indicative of a rate
or characteristic time of change.

Curves at the same shear rate with different
previous histories are displaced varying distances
from the steady state. This is interpretable in terms
of previous structure. The bigger the structural change
from previous shear to present, the further the curves
are displaced from the steady value.(at the present shear
rate). Experiments where the fluid was previously at
the highest shear rate (the lowest structure) show curves
whose F' is smallest. Figure 16A shows the variation of
F' (at t =0) as a function of shear rate for three different

previous histories. These curves represent the changes
of a few structural levels as a function of shear rate.
Figure 16B gives the variation in F' (at t =0) at different
shear rates as a function of the previous shear rate. The
fluid had attained a steady value at these previous shear
rates. Quantitative analysis like that used for the break-
down curves was not applied. The results would show
changes in slopes and initial values as functions of
previous history and present shear rate as in the break-
down case. The interpretation of these changes would
be similar to that of the breakdown case, and quantitative
description, although more feasible, would yield limited
results. Transformation of the buildup data into curves
of constant structure would be far more useful and enlight-
ening. Consequently this approach was taken, and discussion
follows in a subsequent division of this section.

Figure 16-A

⊙ - previous ss @ 1260 sec^{-1}

x - previous ss @ 630 sec^{-1}

▣ - previous ss @ 420 sec^{-1}

$F'_{t=o}$

D, present (sec^{-1})

D, previous (sec^{-1})

Figure 16-B

⊙ - 8 sec^{-1}

x - 70 sec^{-1}

▣ - 210 sec^{-1}

▼ - 420 sec^{-1}

$F'_{t=o}$

Figure 17

⊙ – previous ss @ 1260 sec^{-1}
x – previous ss @ 420 sec^{-1}
▣ – previous ss @ 70 sec^{-1}
▼ – previous ss @ 24 sec^{-1}

D = 8 sec^{-1}

F"

time, seconds

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2

100 200   400   600   800   1000   1200

Figure 18

Figure 19

⊘ − previous ss @ 1260 sec^{-1}
x − previous ss @ 630 sec^{-1}
⊡ − previous ss @ 420 sec^{-1}
▼ − previous ss @ 210 sec^{-1}
   D= 70 sec^{-1}

time, seconds

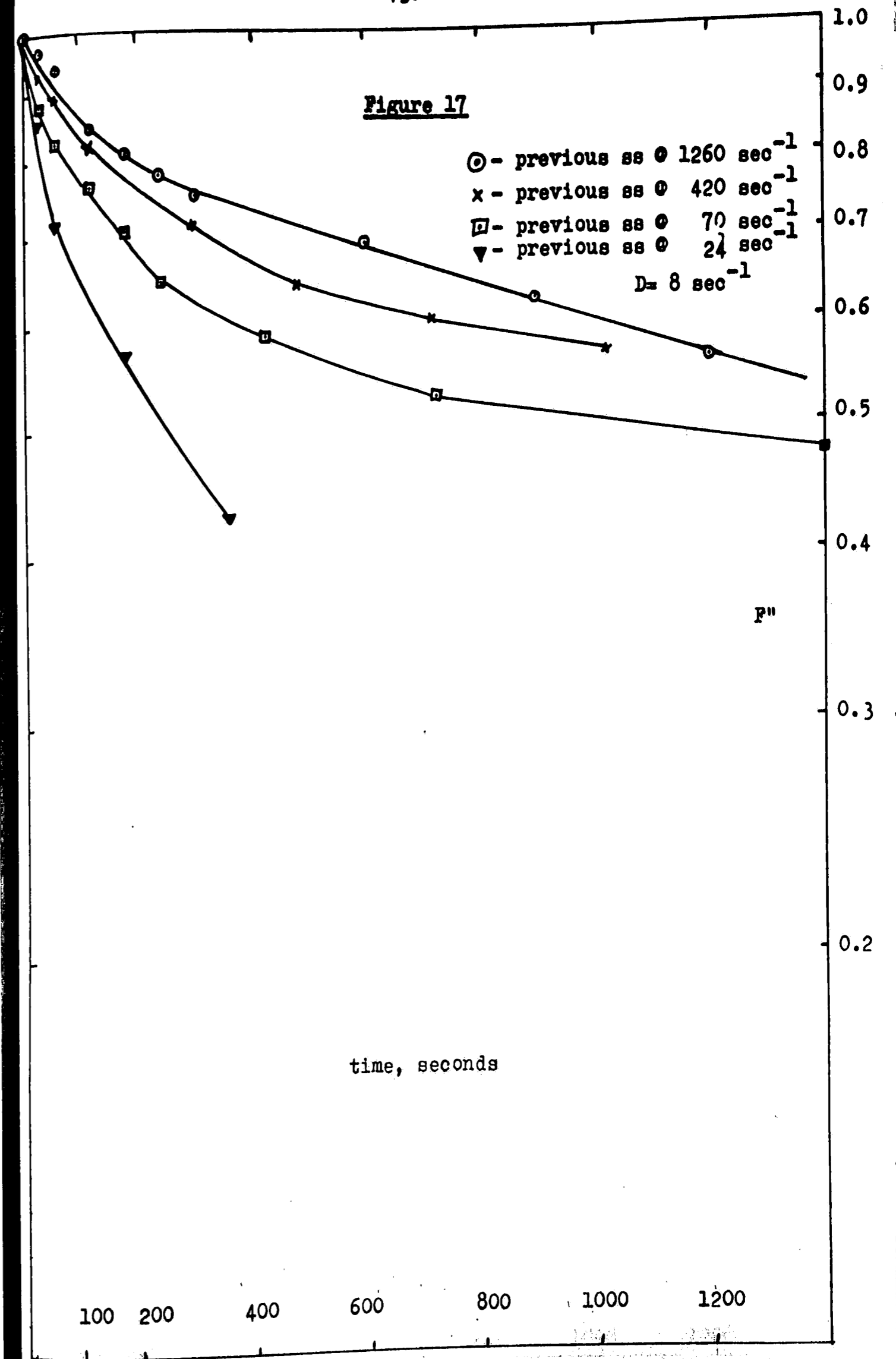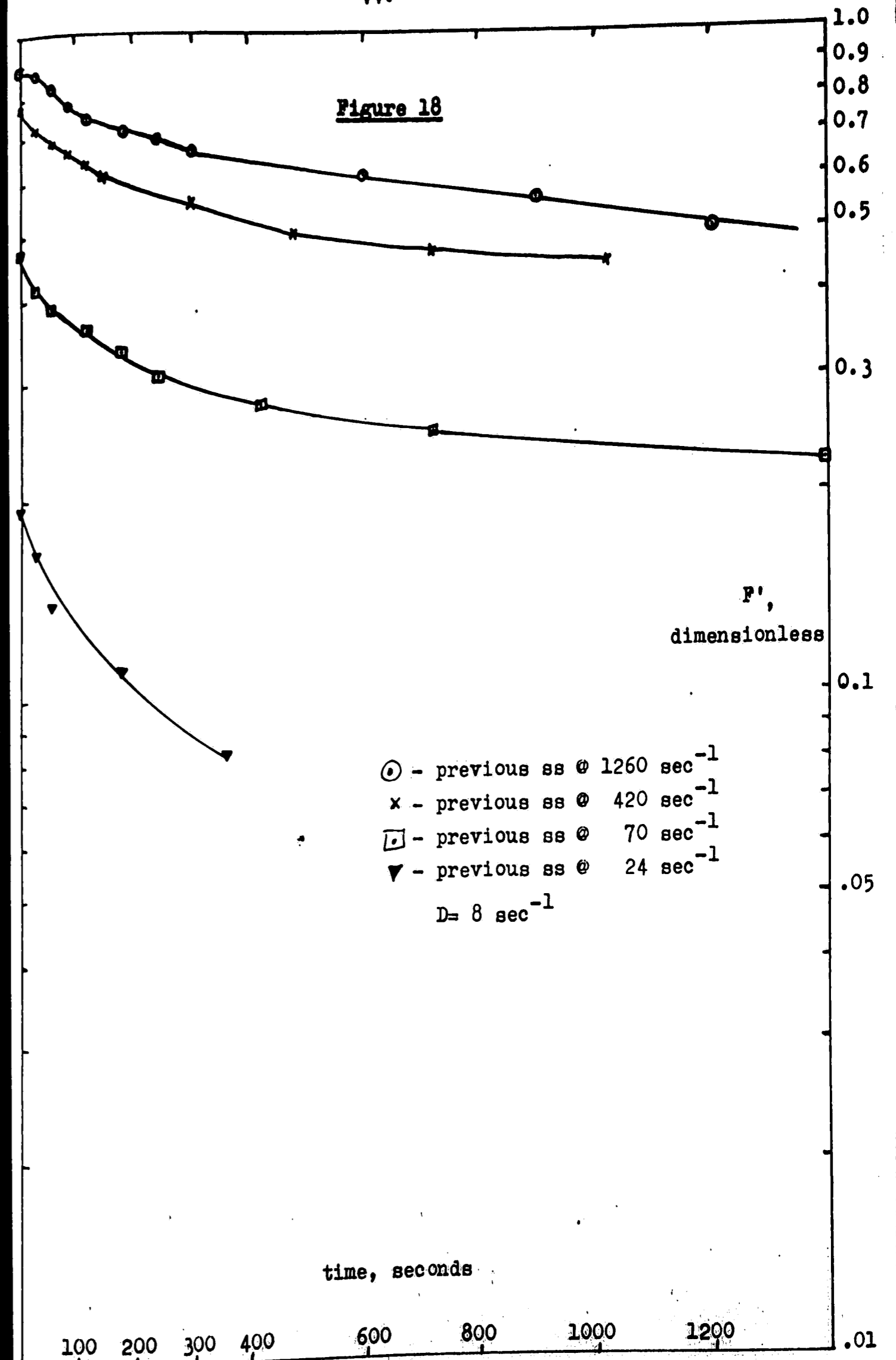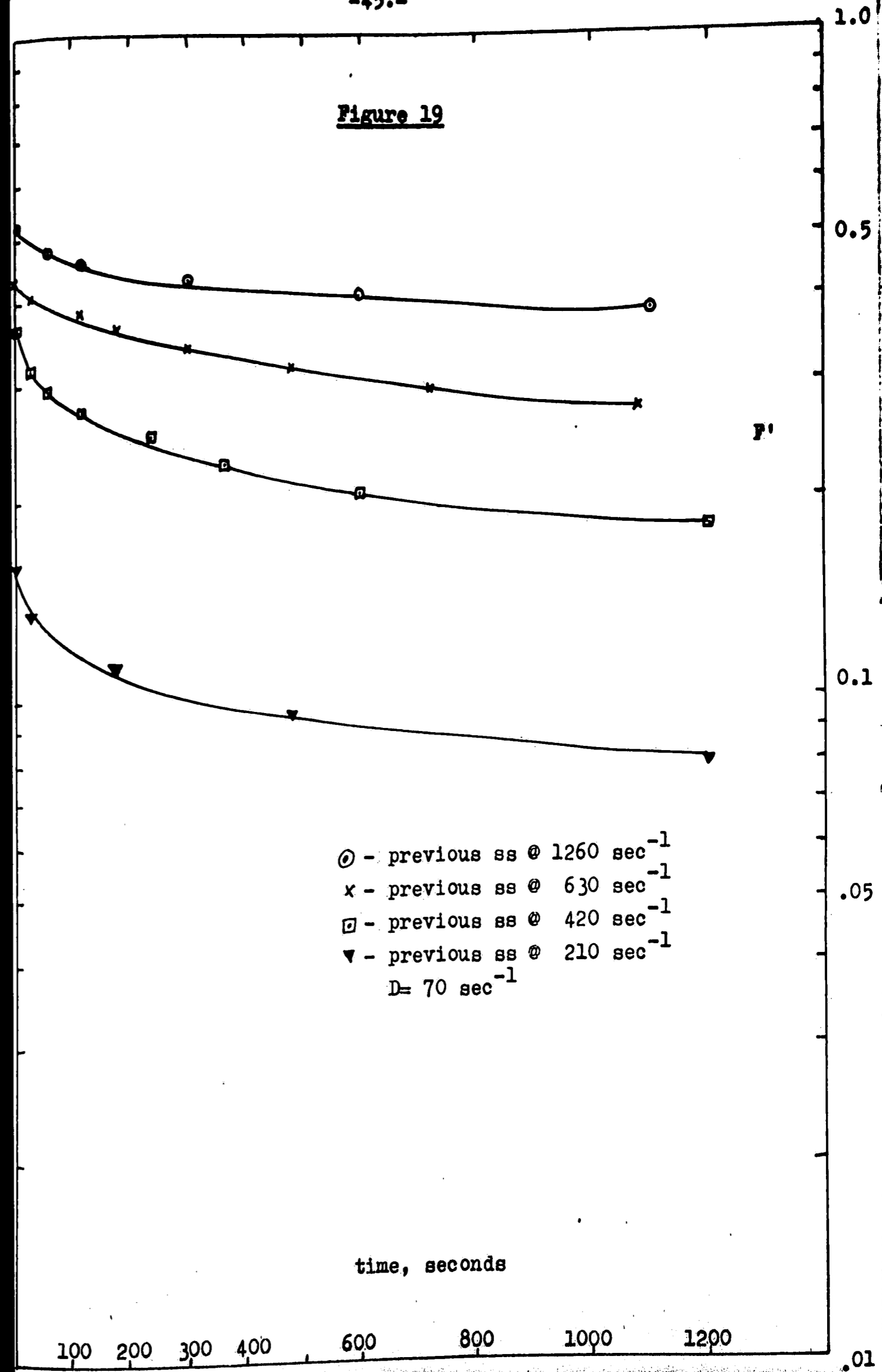## Loop Experiments

Thixotropic loops obtained in these experiments were not generated by the slowly varying flow technique because of peculiarities explained in the Experimental section. The loops were generated with the upcurve closely approximating the steady state flow curve and the downcurve closely approximating a constant structure curve. The upcurve lies above the downcurve in all cases reported herein (Figures 20- 22, inclusive). Since the downcurve is not a straight line, the curves of constant structure are non- Newtonian. This fact supports the conclusion from other evidence that constant structure curves are non- Newtonian.

Quantitative comparison of loops with the breakdown curves is not possible because of the loop generation technique. Table IV shows the results of an attempt to classify thixotropic fluids by two different methods. The first method, $1/m_o$, attempts to classify thixotropic fluids according to their rate of change during the early response to constant shear. The second method, $(F_p-F_{ss})/F_{ss}$, indicates the total change from rest history (or gel state) to the steady state at one constant shear rate. Neither of these methods is quite as effective as the loop technique in classifying thixotropic fluids, but both methods are instructive. Thixotropic fluids must be characterized in terms of total change in structure, rate of change, and response at different shear rates and at different previous histories. The loop test comes closest to putting all these factors together. But the best way to classify thixotropic fluids is through the use of structural levels. This area has hardly been touched to date. When structural levels can be predicted, the total thixotropic change properties of the fluid will be known. Investigating the

TABLE IV

Comparison of rest history breakdown for different fluids at 140 sec^{-1}.

Fluid	$1/m_0$	$(F_p - F_{ss})/F_{ss}$
1.0% cmc	9.8 sec	.077
1.5% cmc	8.5 sec	.195
paint	5.9 sec	.940
mayonnaise	4.5 sec	.358
Clay 4	2.1 sec	6.000

changes in structural levels as a function of shear rate
and previous history should make clear the remaining
factors necessary for complete characterization and
classification of thixotropic fluids.

From Table IV it would appear that the larger the
values of $(F_p-F_{ss})/F_{ss}$, the more thixotropic the fluid.
Similarly, a quicker response or smaller time constant
$(1/m_o)$ would indicate a larger thixotropic nature.
The loop data show some discrepancy, however. The paint
has a much smaller loop area than expected from the values
in Table IV. This can be explained as follows: Practically
all of the thixotropic structure was broken, after a
steady state at the lowest shear rate had been reached.
Subsequent application of shear had little effect, because
there was little thixotropic structure remaining in the
fluid. The peak heights for the paint in Table V are
very close to the steady state stress value. This indicates
very little change in the structure as a result of
application of constant shear rate. The paint was a
commercial latex but did not support its own weight when
inverted in a tube. The original thixotropic nature could
have been degraded somewhat by aging.

TABLE V

Peak heights and yield values from loop generation.

shear rate, sec^{-1}	Peak heights, dynes/cm^2				
	1.0% cmc	1.5% cmc	paint	Clay 4	Mayonnaise
8	104	410	154	87	695
24	170	460	203	105	775
48	236	610	322	125	1020
70	280	720	420	135	1150
140	404	950	660	157	1590
420	645	1420	1350	284	2710
630	760	1590	1520	417	3020
1260	1040	2000	2530	620	3960
yield strength, dynes/cm^2	0	17.4	11.6	78.1	394.0

Figure 20

Clay 4

Figure 21

Cmc

Figure 22

Mayonnaise

paint

F,
dynes/cm^2

D, sec^{-1}

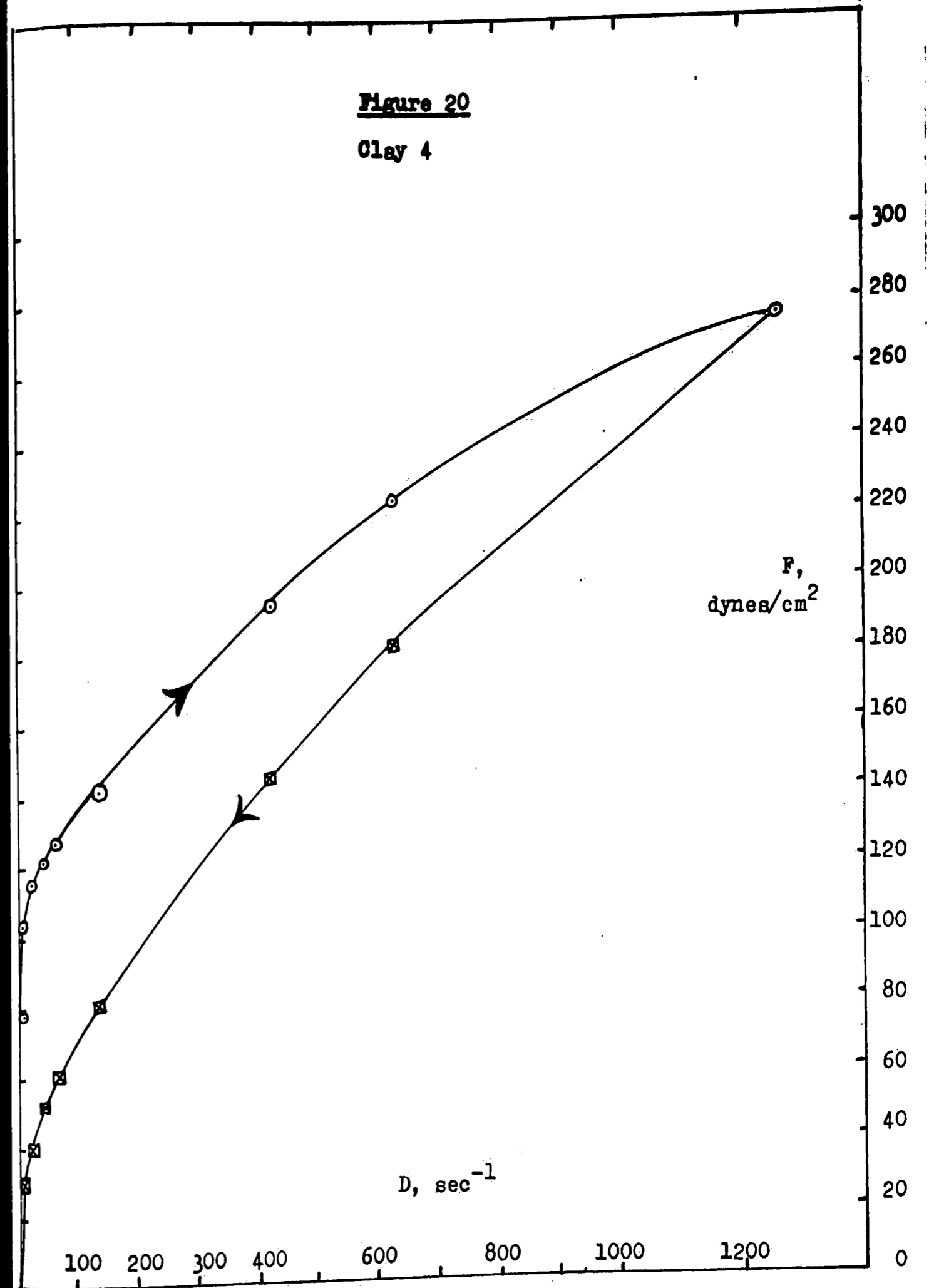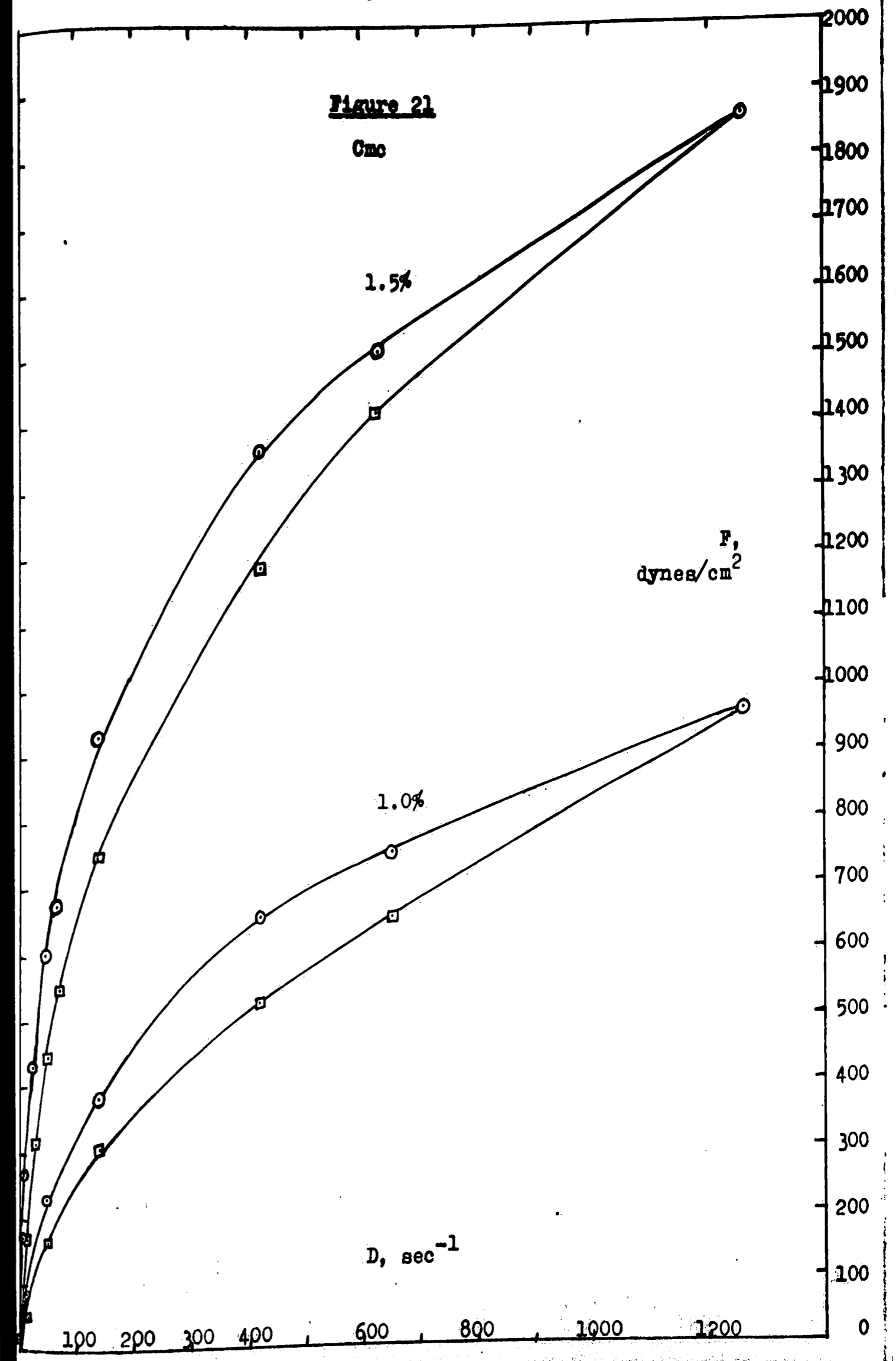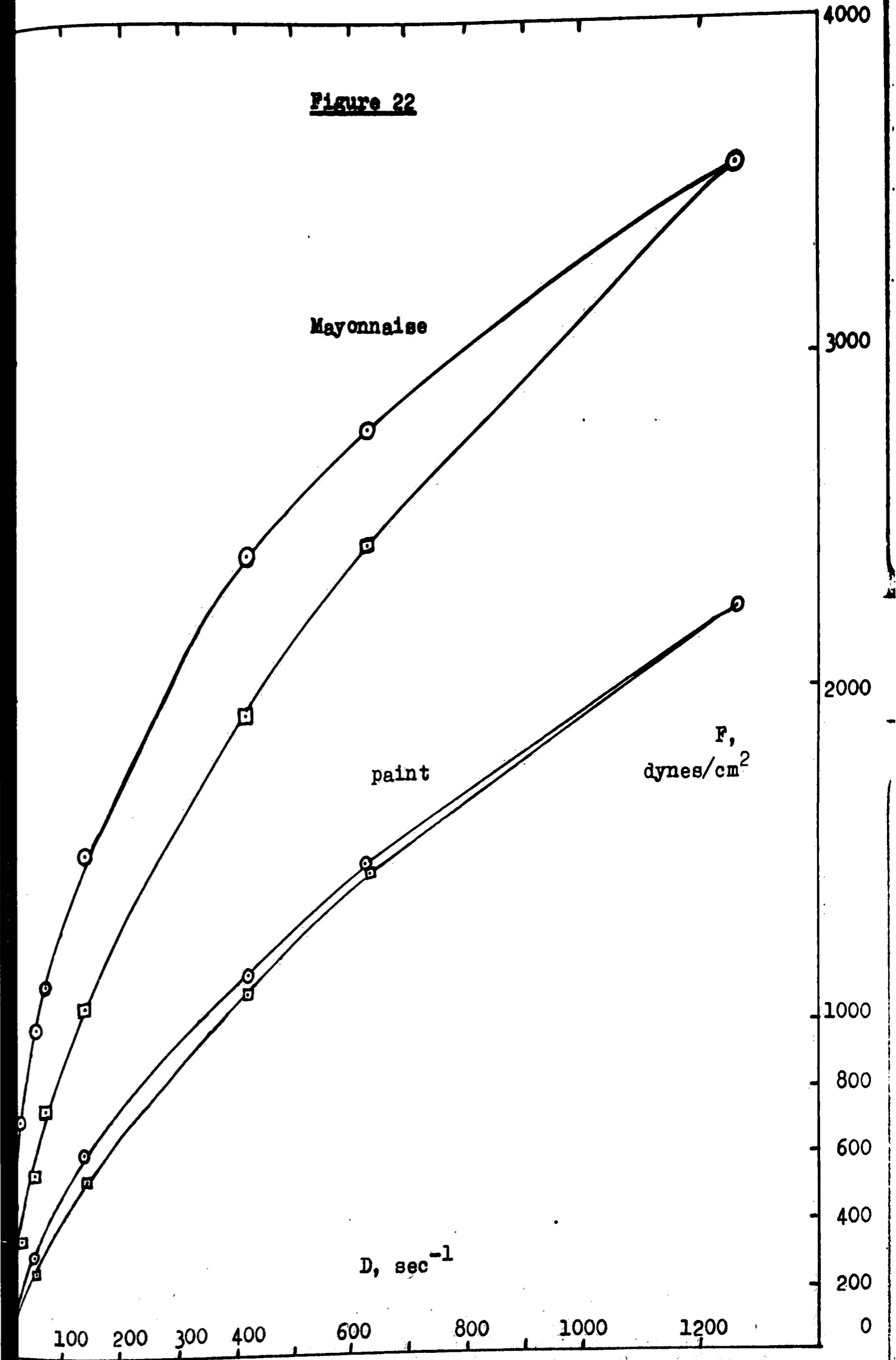## Curves of Constant Structure

Curves representing the same structural state were
obtained from the raw data by selecting the initial values
of various buildup curves, all of which had identical
previous states. Buildup curves at 8, 24, 70, 210, 420,
and 630 sec^{-1} were generated by changing the shear rate
to these values from the steady state stress value
(275 dynes/cm^2) at 1260 sec^{-1}. In a similar fashion
curves of constant structure corresponding to the steady
stress at 630 and 420 sec^{-1} were generated from the experi-
ments at those particular key shear rates. These data
are summarized in Table VI.

A plot of these different levels in comparison with
the steady state flow curve is shown in Figure 23. The
structure levels show power law behavior for shear rates
greater than 24 sec^{-1}. The power law model contains two
constants, K and n. The stress is a function of the shear
rate as F= KD^n. The constant "n" is obtained from the
slope of the line on a plot of log F vs. log D. The
structure curves for the top four shear rates all had the
same slope. The value of "n" was found to be 0.576.
The value of "K" was found by replotting the data as
F vs. D^n and taking slopes. The curves deviated from linear
behavior at the lower shear rates (Figure 24). The values
of "K" were found to increase with increasing structure.
When the "K" values were plotted vs. log (1/D), markedly
linear behavior was observed (Figure 25). The value of
"D" for a particular "K" was chosen as that value at which
the constant structure curve intersected the steady state
flow curve. There were four levels of constant structure
in the power law region as determined by the available
shear rates. Each level is characteristic of a certain
shear rate. In this case each level corresponded to the

TABLE VI

Initial stress values from buildup as a function previous history and present shear rate for structure level studies.

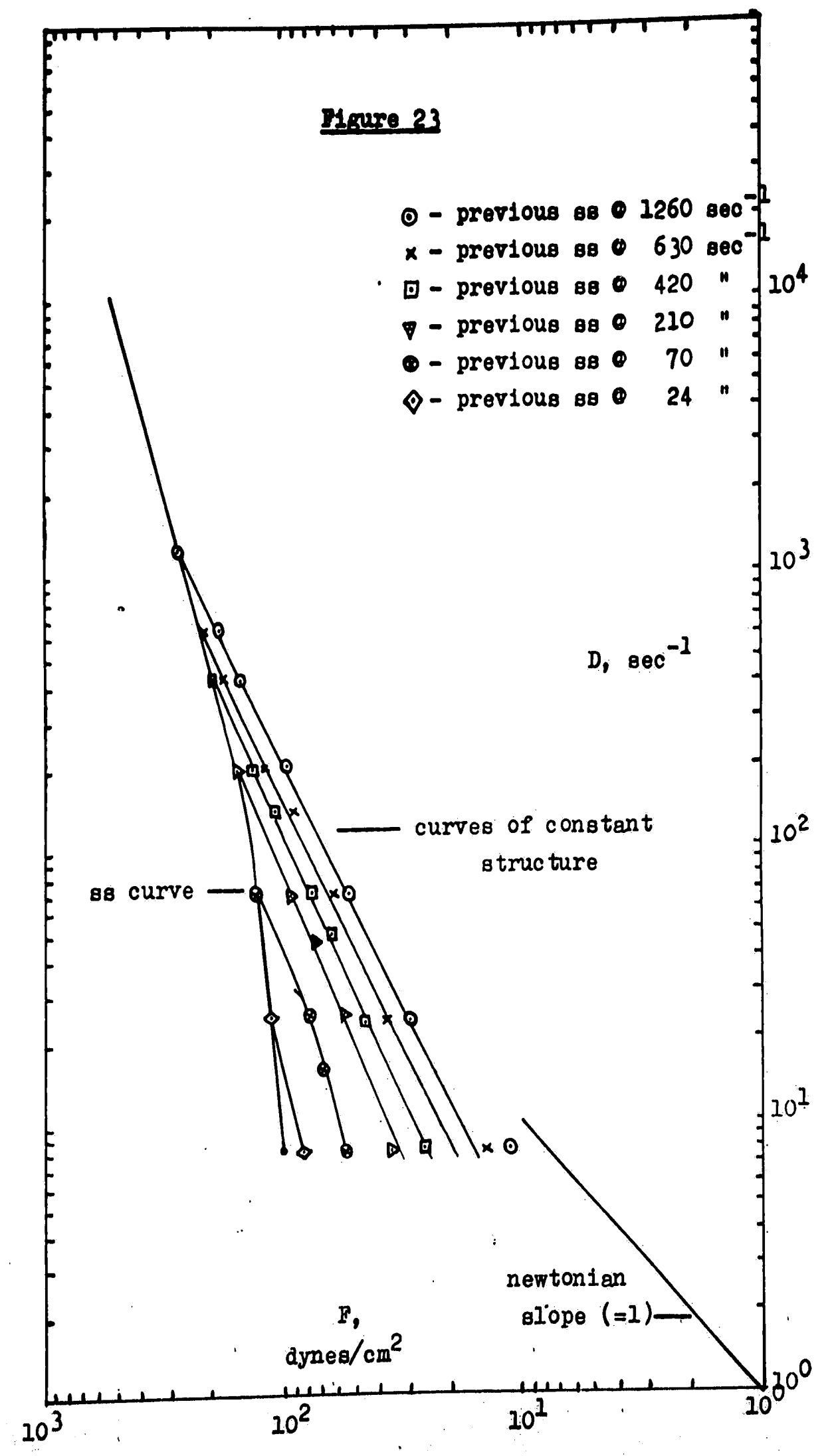|	present shear rate, $\sec^{-1}$								
	8	24	48	70	140	210	420	630	1260
F_{ss}, dynes/cm^2	104	116	122	128	142	152	191	223	275
$F_{t=0}$, equiv. to ss@ 1260	11.5	30.5	--	54	--	101	151	190	275
$F_{t=0}$, equiv. to ss@ 630	14.5	38.0	--	64	93	122	180	223	
$F_{t=0}$, equiv. to ss@ 420	26.0	46.5	64	78	110	136	191		
$F_{t=0}$, equiv. to ss@ 210	35.0	55.0	74	93	152				
$F_{t=0}$, equiv. to ss@ 70	55.0	76.0	--	128					

Figure 23

Figure 24

Plot to obtain "K" values

F, dynes/cm^2

⊙ - corresponds to ss @ 1260 sec^{-1}
× - corresponds to ss @ 630 sec^{-1}
⊡ - corresponds to ss @ 420 sec^{-1}
▽ - corresponds to ss @ 210 sec^{-1}

D^n, (sec^{-1})^n
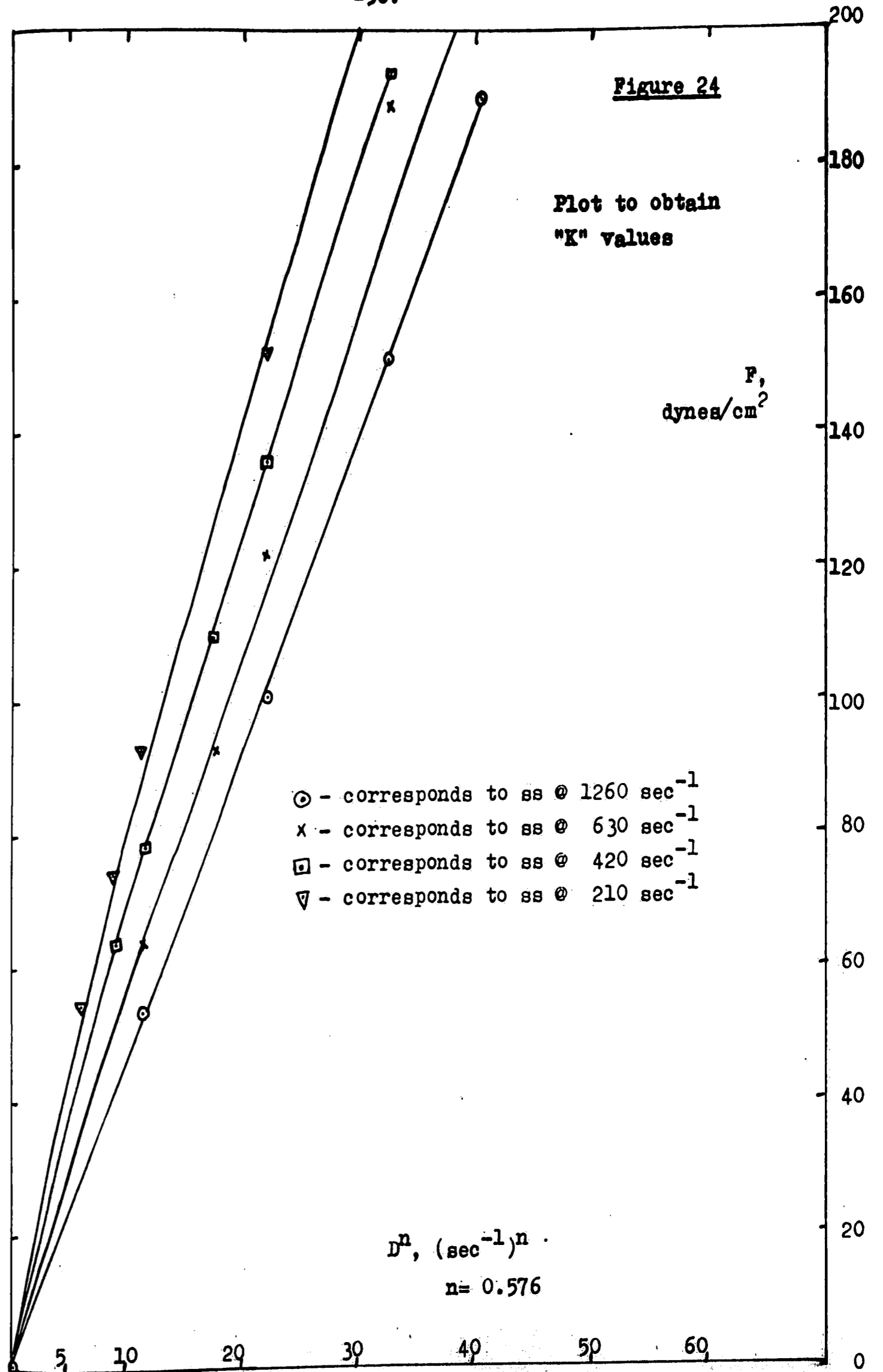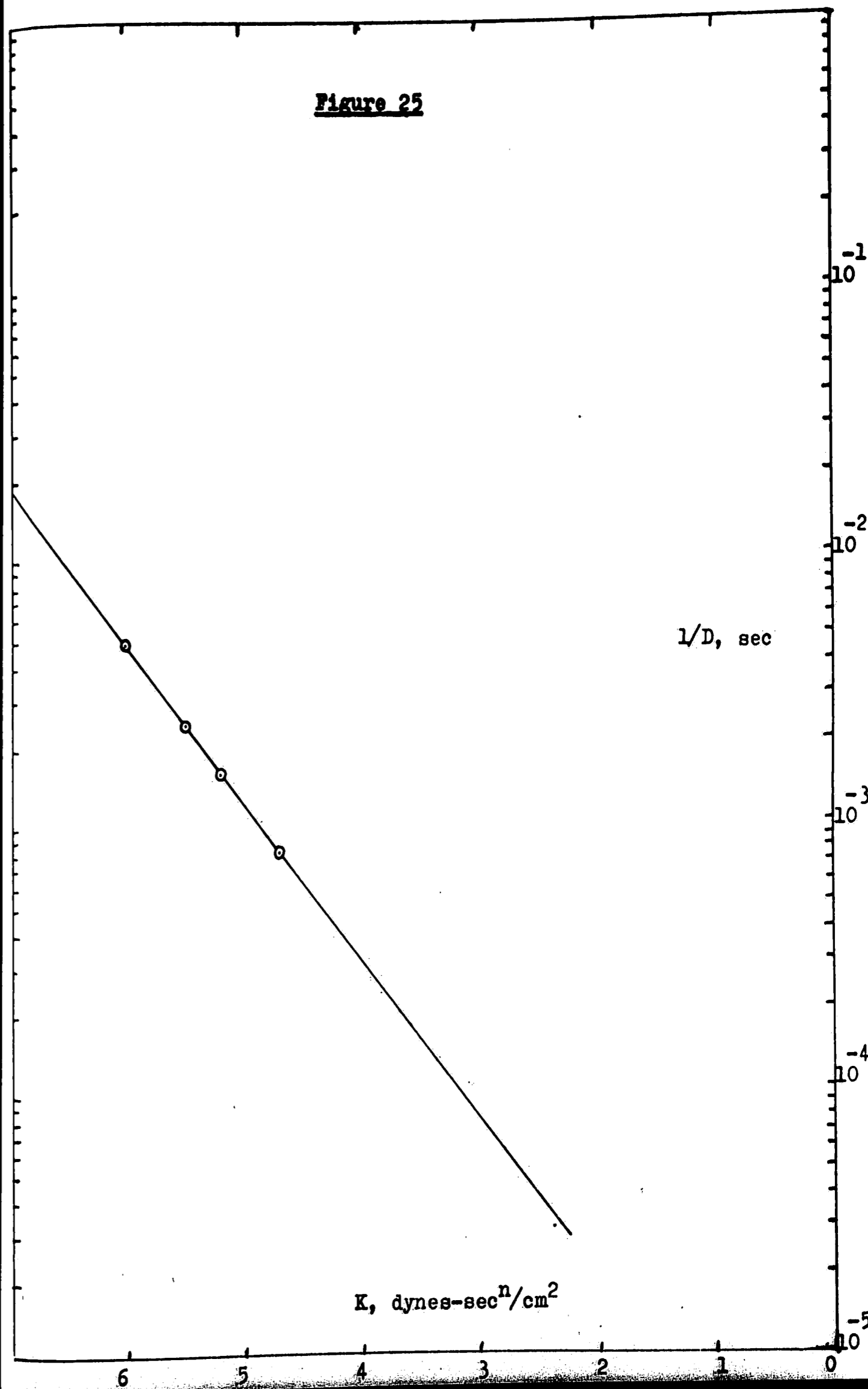$n = 0.576$

Figure 25

$1/D$, sec

K, dynes-sec^n/cm^2

steady stress values at four different shear rates
(1260, 630, 420, 210 sec^{-1}). Each level had a character-
istic "K" value. Figure 25 shows how this "K" value
varies with the characteristic shear rates for the four
different structural levels. The structure with the
highest characteristic shear had the lowest "K" value
and the lowest structure. Therefore the "K" values are
a measure of the structural levels within the fluid. It
seems reasonable at this stage to postulate that the
structure will be zero when K= 0. Figure 25 can predict
the shear rate corresponding to a steady state at which
this occurs. This means that if a thixotropic fluid is
sheared from rest history at the shear rate at which K= 0,
the structure will change from 100% to 0%.

With the information presented here, any structural
level below the steady state flow curve can be calculated,
as long as the levels remain in the power law region. If
a level is to be generated corresponding to a steady state
stress at D_1, a simple procedure will supply the necessary
information. Figure 25 will give the "K" value for the
structure corresponding to the steady stress value at
D_1. It is presumed that "n" is known, and that F= KD^n.
Values for $D \angle D_1$ are picked and the corresponding F's
calculated and plotted. The resulting curve is a curve
of constant structure. The structure along this curve is
the same as that for the steady stress value at D_1.

Curves of constant structure from the literature (6)
were subjected to the "K- n" treatment. It was very
difficult to select values of "F" and "D" from the curves
with any accuracy. Cheng's fluid was extremely shear thinning,
and only two of the three reported levels were in the
power law region. The results of the analysis are
summarized in Figures 26- 28, inclusive. The procedure
seems to work, even though the accuracy is open to question.

Figure 26

Cheng's data

ss curve

constant
structure curves

$F,$
dynes/cm^2

10^3

10^2

D, sec^{-1}

10^2 10^3

Figure 27

260

250

240

F,
dynes/cm^2

220

210

200

190

180

170

160

150

x — corresponds to
ss @ 380 sec^{-1}

140

⊙ — corresponds to
ss @ 2,000 sec^{-1}

130

120

D^n, (sec^{-1})^n
n= 0.44

.2   .4   .6   .8   1.0   2.0

Figure 28

1/D, sec

K, dynes-sec^n/cm^2

600   500   400   300   200   100

10^{-1}

10^{-2}

10^{-3}

10^{-4}
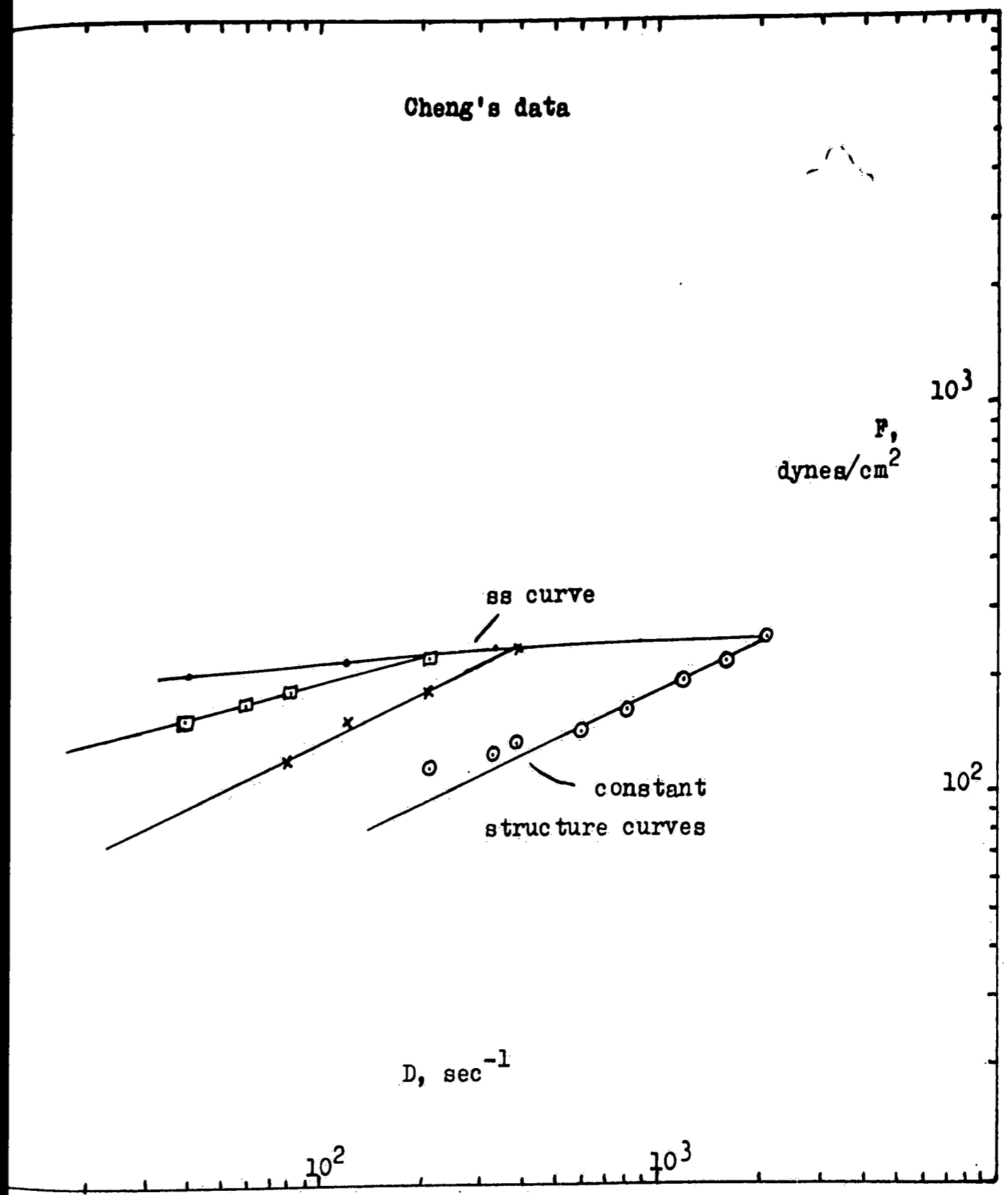
Other Experimental Results

Yield values for the respective thixotropic fluids were obtained according to Heinz (15). These values have been tabulated along with the loop data in Table V.

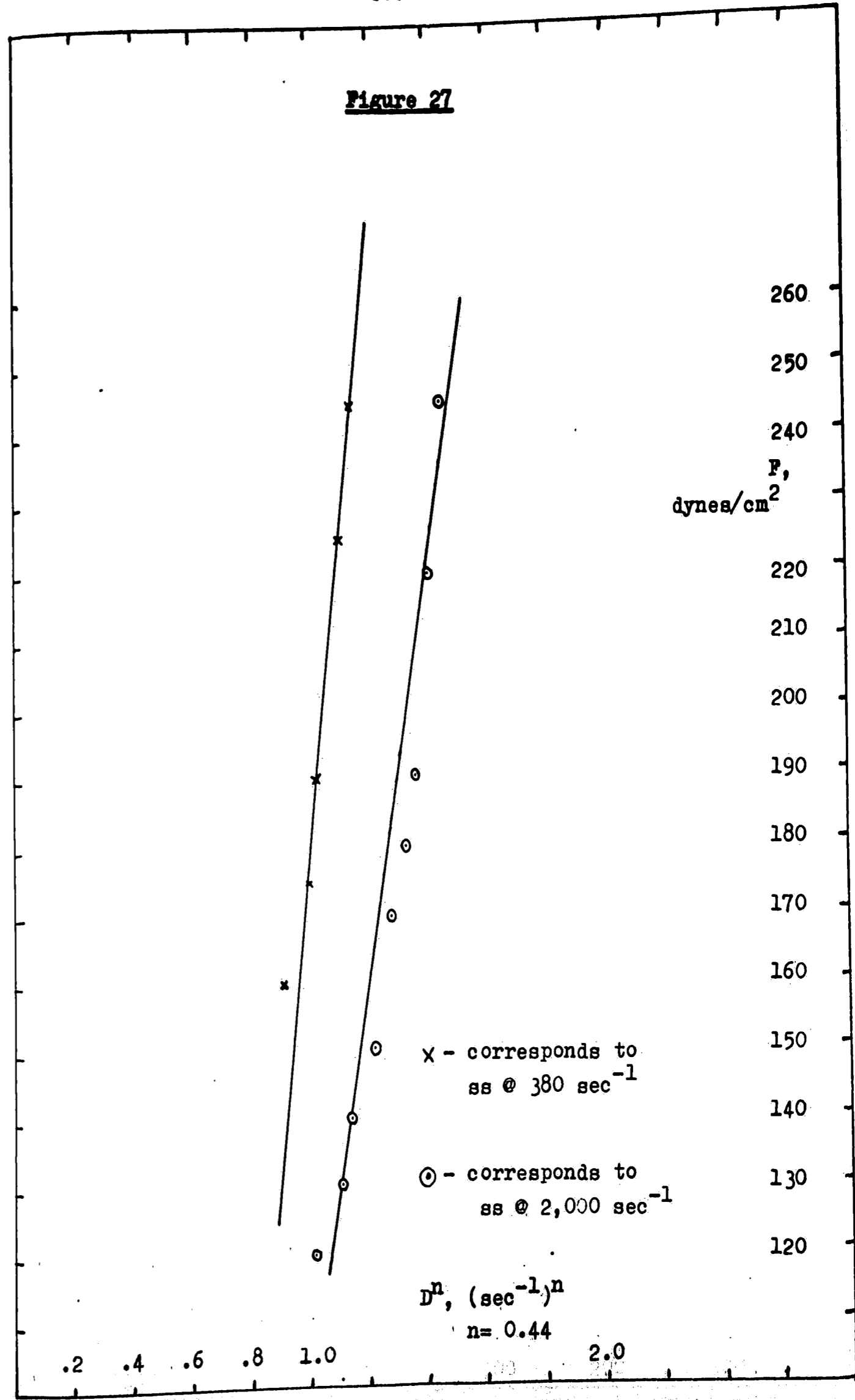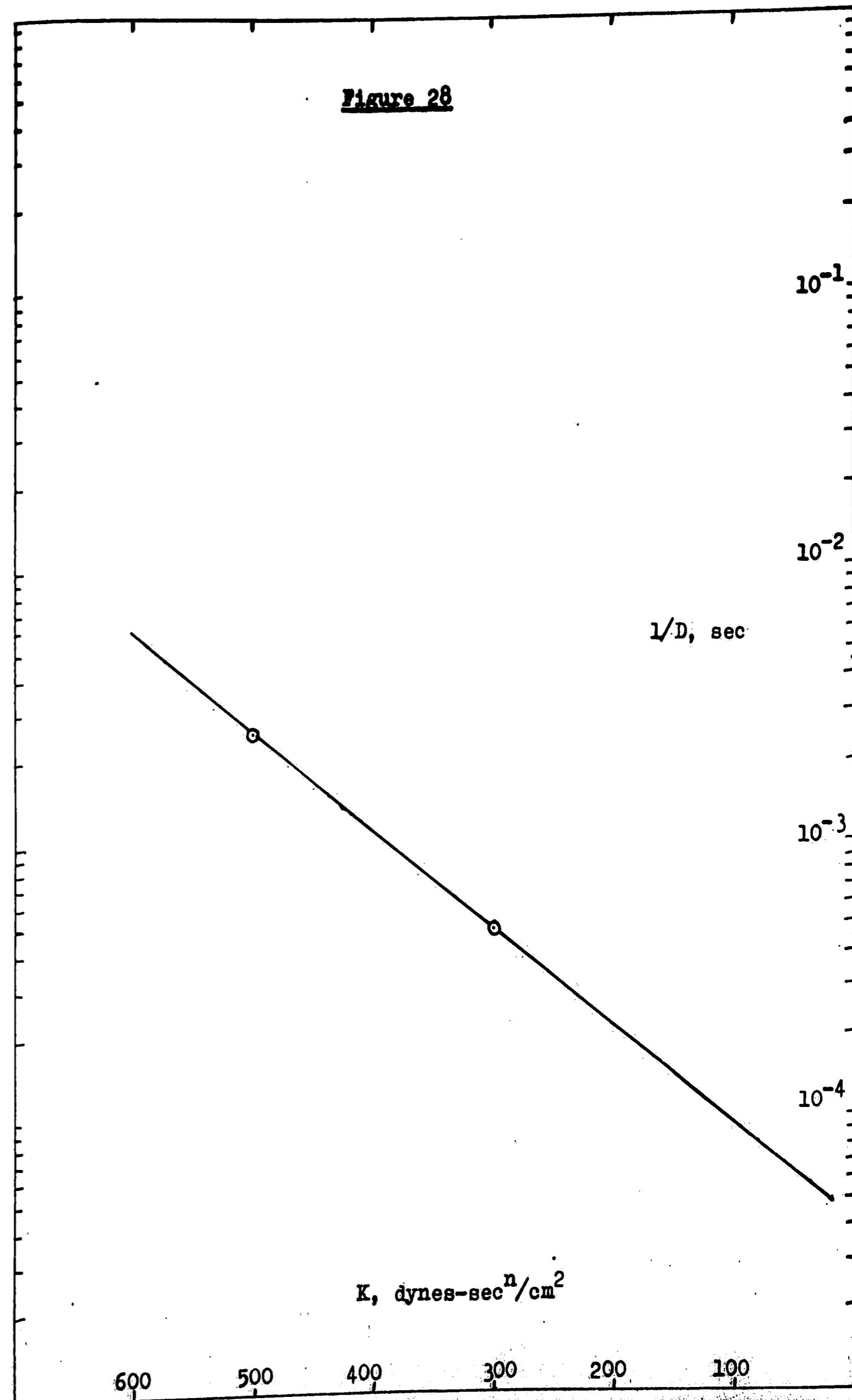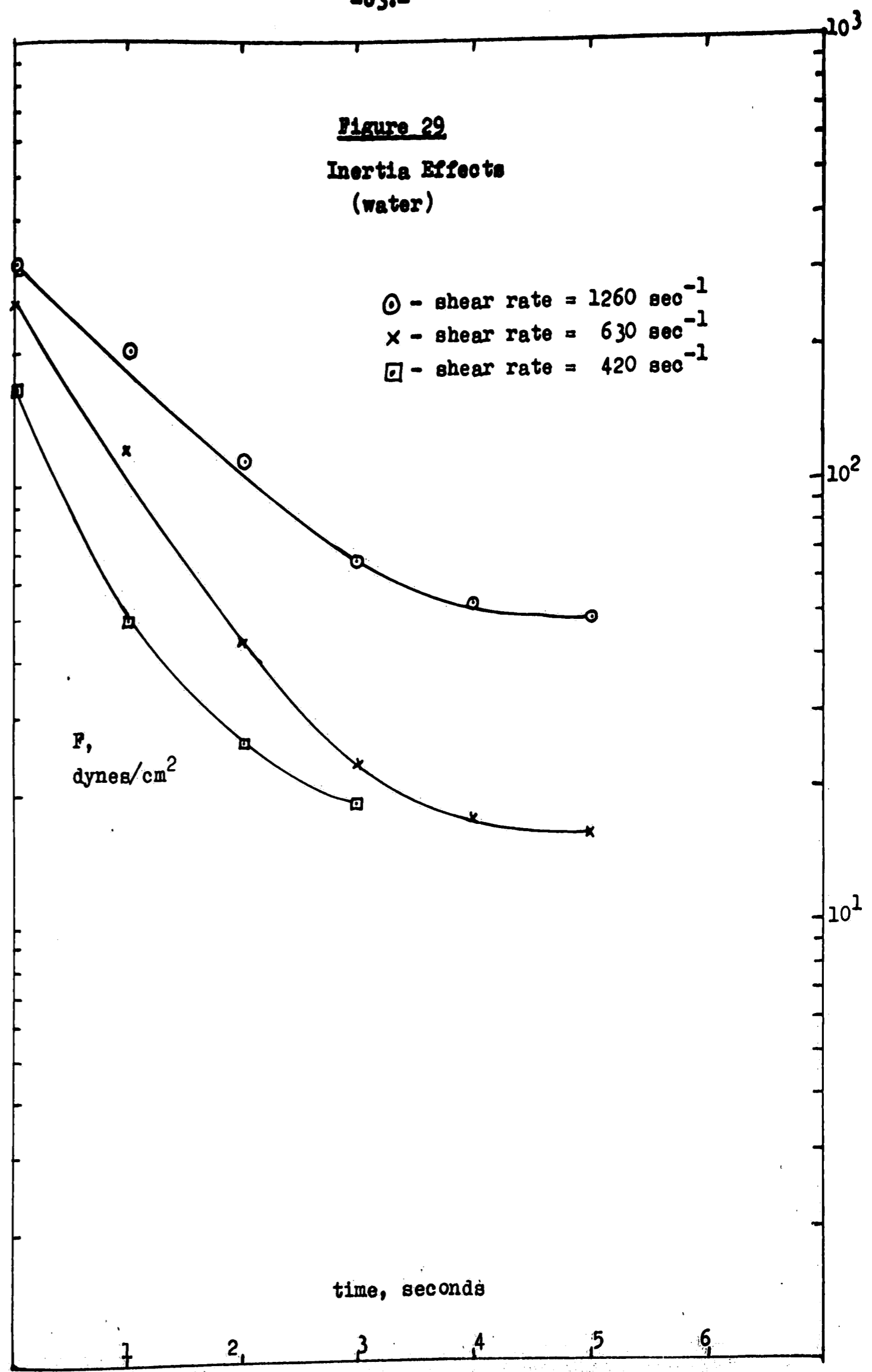Inertia curves for water at different shear rates are given in Figure 29. The other fluids tested had much higher viscosities than water. Because of their higher viscous resistance these fluids would tend to damp out the inertia effects in the cup and bob faster than water. The extent to which this actually occurred is unknown. Consequently interpretation of the early portion of the breakdown curves at the higher rates of shear is open to some debate.

At this point it seems appropriate to discuss one of the mystifying observed experimental facts. The allusion is in reference to the program summarized in Figure 30. The fluid was sheared to a steady state, whereupon the shear rate was then changed to a lower value. The fluid was allowed to build up its structure at this lower shear for about 20 minutes. The shearing was then stopped and re-applied after 20 minutes of rest. Structural rebuilding has taken place both under the lower shear rate and during the resting period. When the shear was resumed, one would expect the behavior represented by curve 2 in Figure 30.

It is clear that the buildup is governed by different time constants which are functions of shear rate. What is characteristic of the fluid's time behavior at one shear rate is not necessarily characteristic at another. Figure 30 is a manifestation of this fact. The behavior can be explained in the following way: When the shear rate was changed to zero, buildup continued. However, this buildup is now characterized by its "zero shear rate time constants". In 20 minutes time it had built up to

Figure 29

Inertia Effects
(water)

⊙ - shear rate = 1260 sec^{-1}
× - shear rate = 630 sec^{-1}
▣ - shear rate = 420 sec^{-1}

F, dynes/cm^2

time, seconds

a structure level above that characteristic of the steady
stress value at the lower shear rate. The breakdown occurs
not merely as the result of shear, but as a result of
the sudden change in the shear rate. In any case the
breakdown curve should have leveled off at the steady
state stress value. It did not. The final value for the
breakdown curve was identical to that of the buildup curve
before shearing was stopped, i.e. below the steady state
stress value. A mechanistic argument must be adopted at
this point.

The buildup is governed by a number of discrete
time constants, each related to a characteristic mechanism.
Only one of these mechanisms seems to have contributed
to the buildup when shearing was stopped. Had the fluid
been allowed to rest for 19 hours and then sheared at the
lower shear rate, a breakdown curve would be generated,
whose final value would be very close to the steady state
stress characteristic for that shear rate. The mechanism
operative for at least the first 20 minutes of zero shear
rate buildup is apparently a framework type mechanism.
The outlines of structure are formed in this period like
the steel girder frame of a building. When shear is
resumed, the framework, being the weakest structural element,
is the first to be destroyed. When all of the structure
resulting from the first 20 minutes of zero shear buildup
has been removed by shear, different mechanisms take over,
and rebuilding commences from the same level it had
previously reached. Hence the breakdown curve at the
lower shear rate levels off at the previous buildup
value. This analysis rests on the fact that buildup and
breakdown curves can be reduced to sums of discrete
components. The buildup mechanisms do not seem related
to the breakdown mechanisms, nor do they seem to follow
in any sort of reverse sequence.

Figure 30
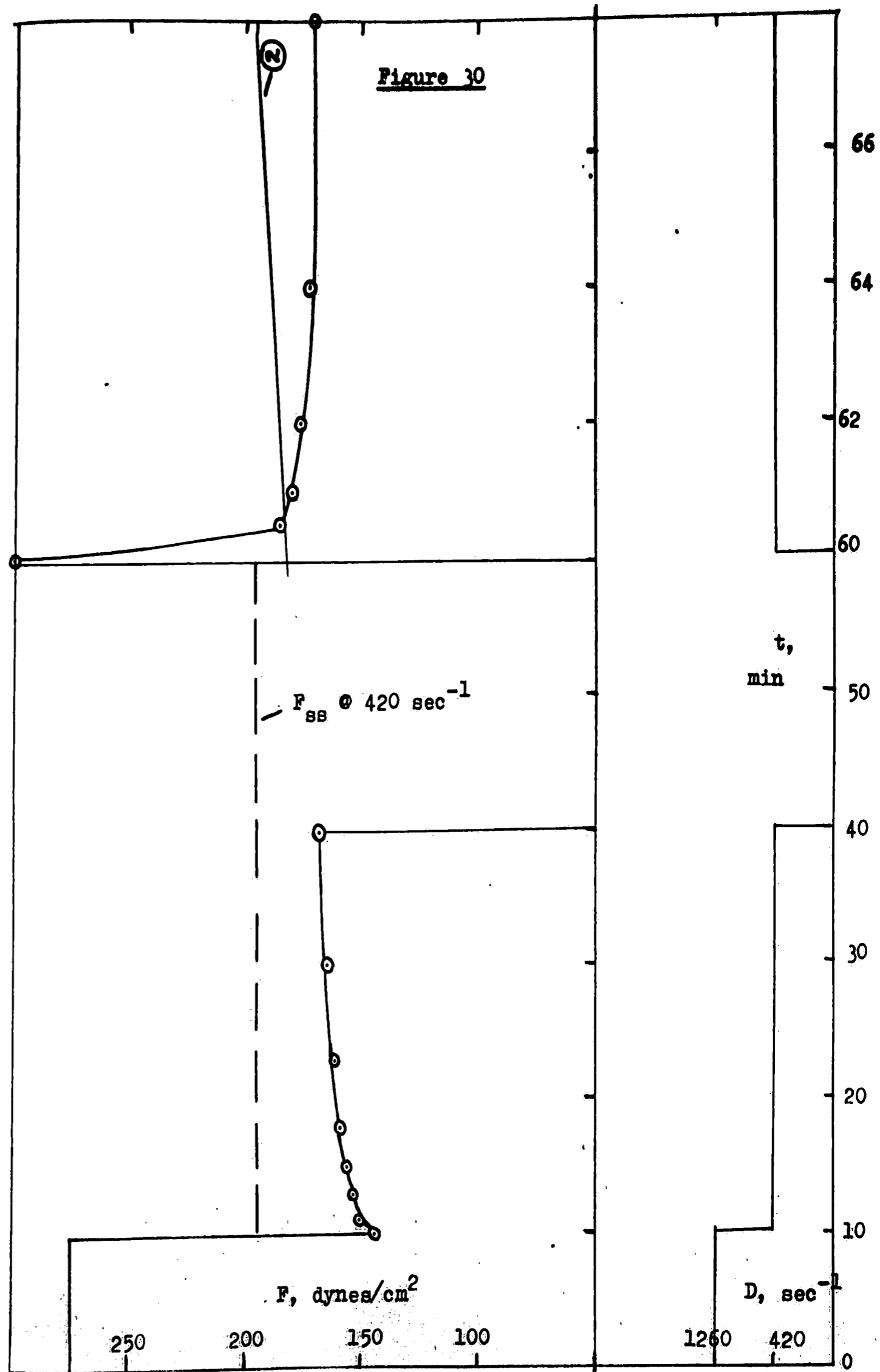
VI. CONCLUSIONS

It is evident from this work that thixotropy is a
very complex phenomenon. The importance of mechanisms
and previous history have been shown. It was virtually
impossible to determine how the time constants of thixo-
tropic change are affected by shear rate and previous
history. The concept of constant structure curves appears
to be the most promising area for future investigation.
Here it is possible to map out any change of a thixotropic
fluid due to shear rate. It should prove most useful in
studying these changes. The following are the conclusions
of this work:

1. There is presently no adequate phenomenological theory
   available to account for the rheological behavior of
   thixotropic fluids. This is a consequence of incomplete
   understanding of the nature of thixotropic change.

2. An exponential series can be used to fit the transient
   stress response to a step change in shear rate for a
   thixotropic fluid. The results indicate that the
   response at a given shear rate is governed by three
   discrete time characteristics. These effects can be
   described in terms of a distribution of rate constants,
   or a spectrum of characteristic time responses analogous
   to viscoelastic theory via Tobolsky. These constants
   are related to characteristic mechanisms of change and
   are not true constants, since they are functions of
   both the applied shear rate and the previous history.
   The functionalities were unable to be determined,
   because the responses appeared to be non- uniform, and
   experimental problems limited the interpretation of
   the results.

3. At long times the rate of change of shear stress is dominated by a single characteristic time, since a plot of log F' vs. t becomes linear in this region. The time constant for this region is a function of present shear rate and previous history.

4. Previous history affects the transient stress curves by shifting them to lower values of stress for increasing shear rate history. The higher the previous shear rate corresponding to a steady state, the lower the structure will be. This manifests itself as a lower stress reading for the transient response.

5. Initial values from the transient stress curves are characteristic of the immediately preceeding structural state of the fluid.

6. The peak values (initial stress values) for Clay 4 did not show any significant variation with present shear rate when rest history breakdown curves were generated. The peak values ranged from 945 to 1040 dynes/cm^2 at 1260 sec^{-1}. An average value of 1010 dynes/cm^2 was used. This result supports Weltmann's observations (33) and is in disagreement with Casey's work (4). These results could have been influenced by inertia effects.

7. The loop data correlate qualitatively with the breakdown data. The paint was an exception for the reasons previously discussed. The loop test is not really useful in analyzing thixotropic fluids, because it cannot separate the different factors involved in thixotropic change. However, it is a good method to determine the overall change properties of the fluid.

8. The transient response of shear stress tends toward
   the same equilibrium point at a given shear rate,
   whether the stress is above or below that point when
   the shear rate is first imposed. This is a verification
   of Goodeve's concept of dynamic equilibrium (12), and
   of rate concepts used by many other investigators (6,10,
   18,21,23,29). However, this conclusion is not indepen-
   dent of previous history as shown in the Discussion
   section of this work. The mechanisms of change are
   very important in determining the structure and conse-
   quently the time response.

9. The structure levels of Clay 4 are non- Newtonian.
   This was shown by observing the downcurve in the
   thixotropic loop experiments, and by plotting the
   initial values of the buildup curves as a function
   of shear rate from the same previous structure. This
   conclusion is characteristic of more than one fluid
   as shown in the loop data, and therefore would be
   characteristic of thixotropic fluids in general.

10. The structure levels in a fluid can be predicted if
    the behavior of one structure level is known. In
    this work structure levels below the steady state
    flow curve were determined and characterized for
    the region exhibiting power law behavior. The levels
    above the steady state flow curve were not determined
    because of difficulties in interpretation of the
    breakdown data, i.e. inertia effects and uncertain
    previous structural states.

VII. RECOMMENDATIONS

The recommendations for future work center around the problem of describing structure and its changes. Techniques for obtaining and characterizing structure levels must be developed. Once the structure grid is known and can be predicted, investigation of the changes in structure can proceed. Mechanisms appear to be integrally connected with thixotropic change. The design of proper experiments and the availability of good equipment with well defined responses are crucial aspects of this research effort.

Application of shear disturbance causes thixotropic change. The mechanisms of change are largely unknown, and they appear to be numerous. An investigation of the low shear rate response should yield some interesting information. The rates of disturbance should be near the same magnitude as the rates of change in these experiments. The results should prove stimulating and enlightening.

Modelling should be deferred until a clearer understanding of structure and the mechanisms of change are made available. Ideally the nature of 100% and 0% structure should be clearly defined and able to be demonstrated by experiment. The buildup phenomenon under zero shear rate needs to be compared with the buildup under non- zero shear rates. This should yield information on how the presence of shear rate affects the response of the fluid.
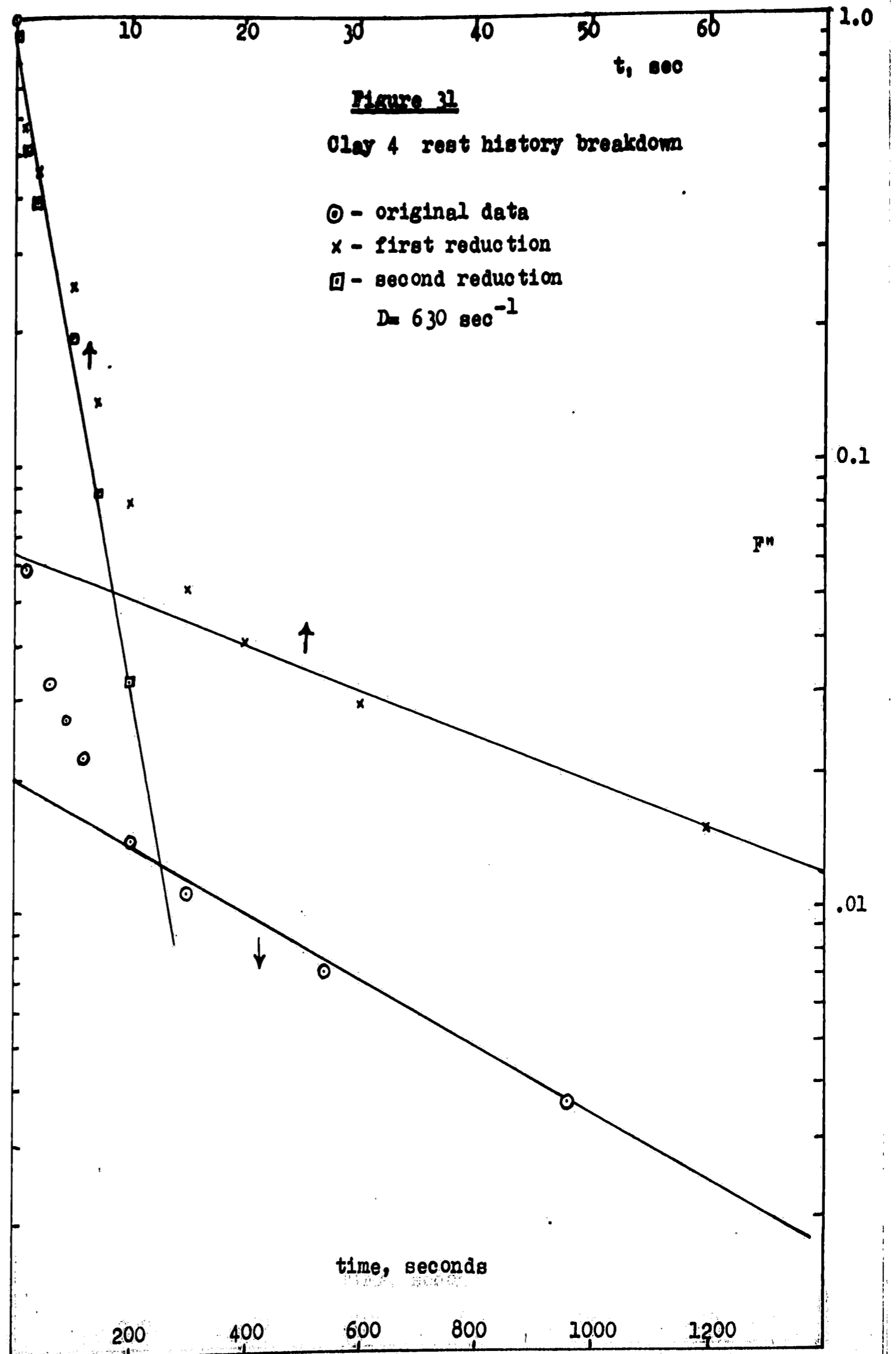
VIII. APPENDIX

A. Additional Data

B. Calculations
1. Procedure X sample calculation
2. Curve fit to data comparison
3. Temperature effects calculation
4. Calibrations and conversion factors

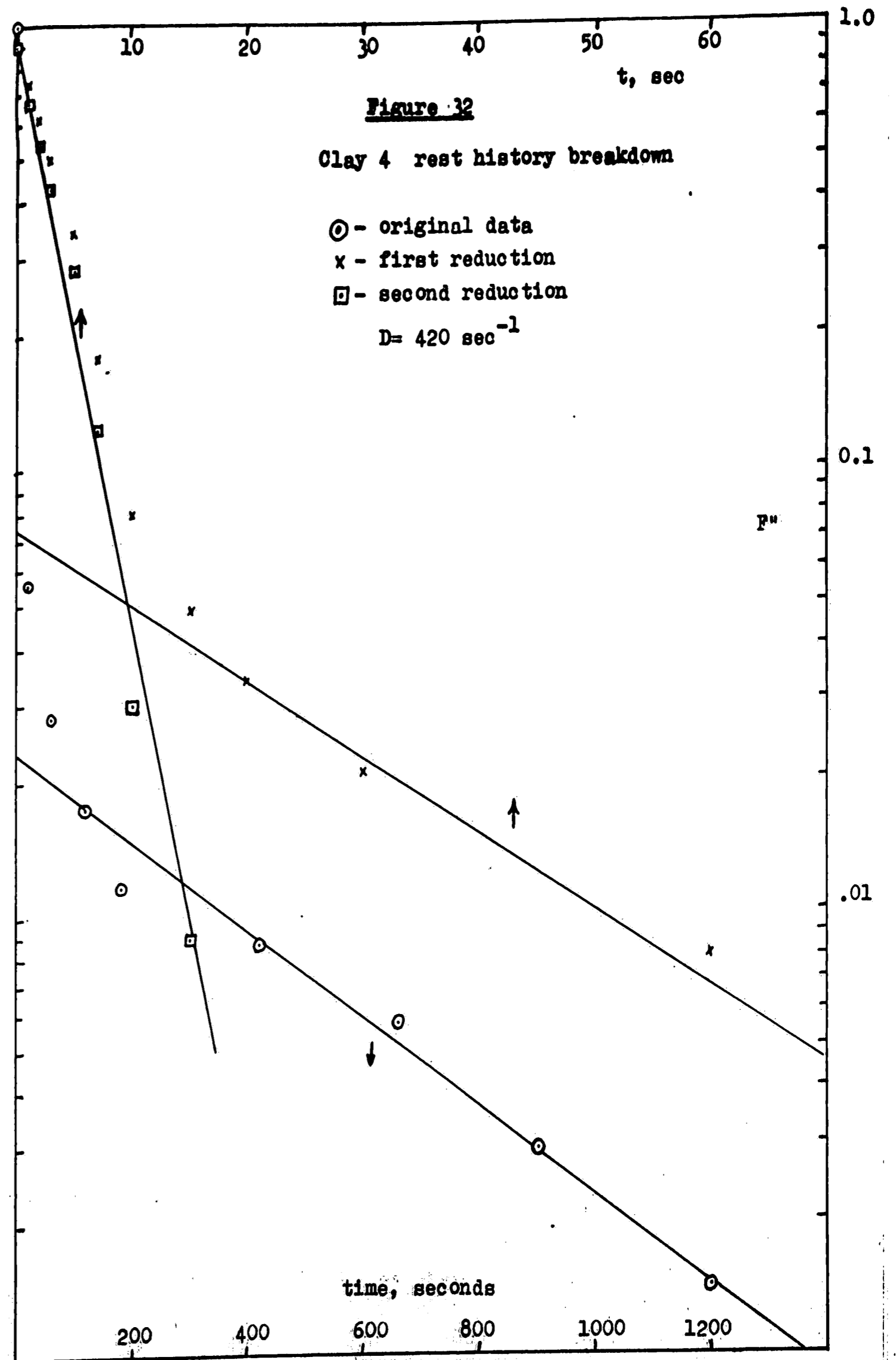C. Material Specifications

D. Equipment Specifications

Figure 31

Clay 4 rest history breakdown

⊙ - original data
x - first reduction
▣ - second reduction
   D= 630 sec^{-1}
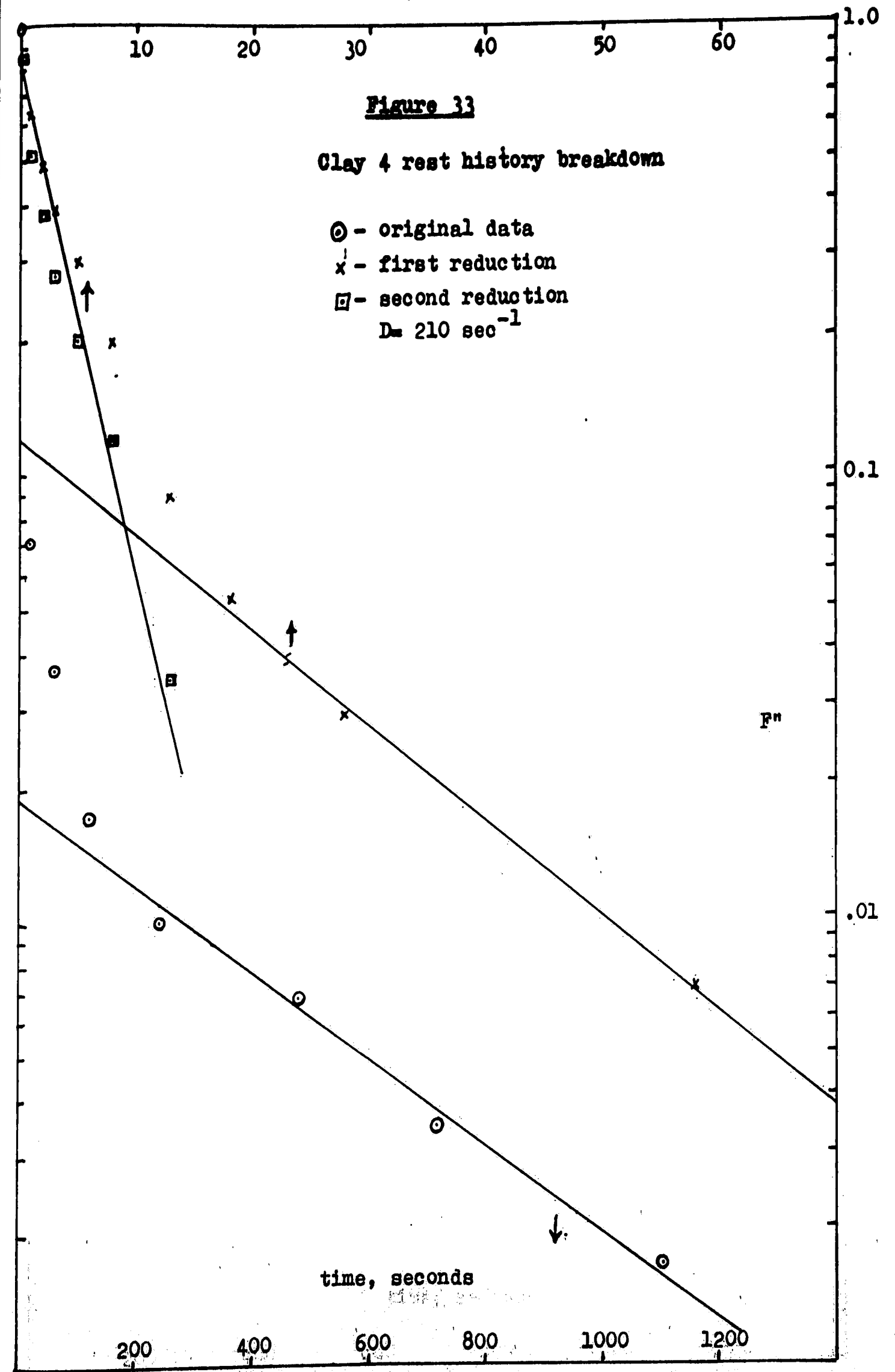
t, sec

F"

time, seconds

Figure 32

Clay 4 rest history breakdown

⊙ - original data
x - first reduction
⊡ - second reduction

$D = 420 \text{ sec}^{-1}$

t, sec

F"

time, seconds

Figure 33

Clay 4 rest history breakdown

⊙ - original data
x - first reduction
▣ - second reduction
$D = 210 \ sec^{-1}$

time, seconds

Figure 34

Clay 4 rest history breakdown

⊙ - original data
x - first reduction
⊡ - second reduction
D= 70 sec^{-1}

time, seconds

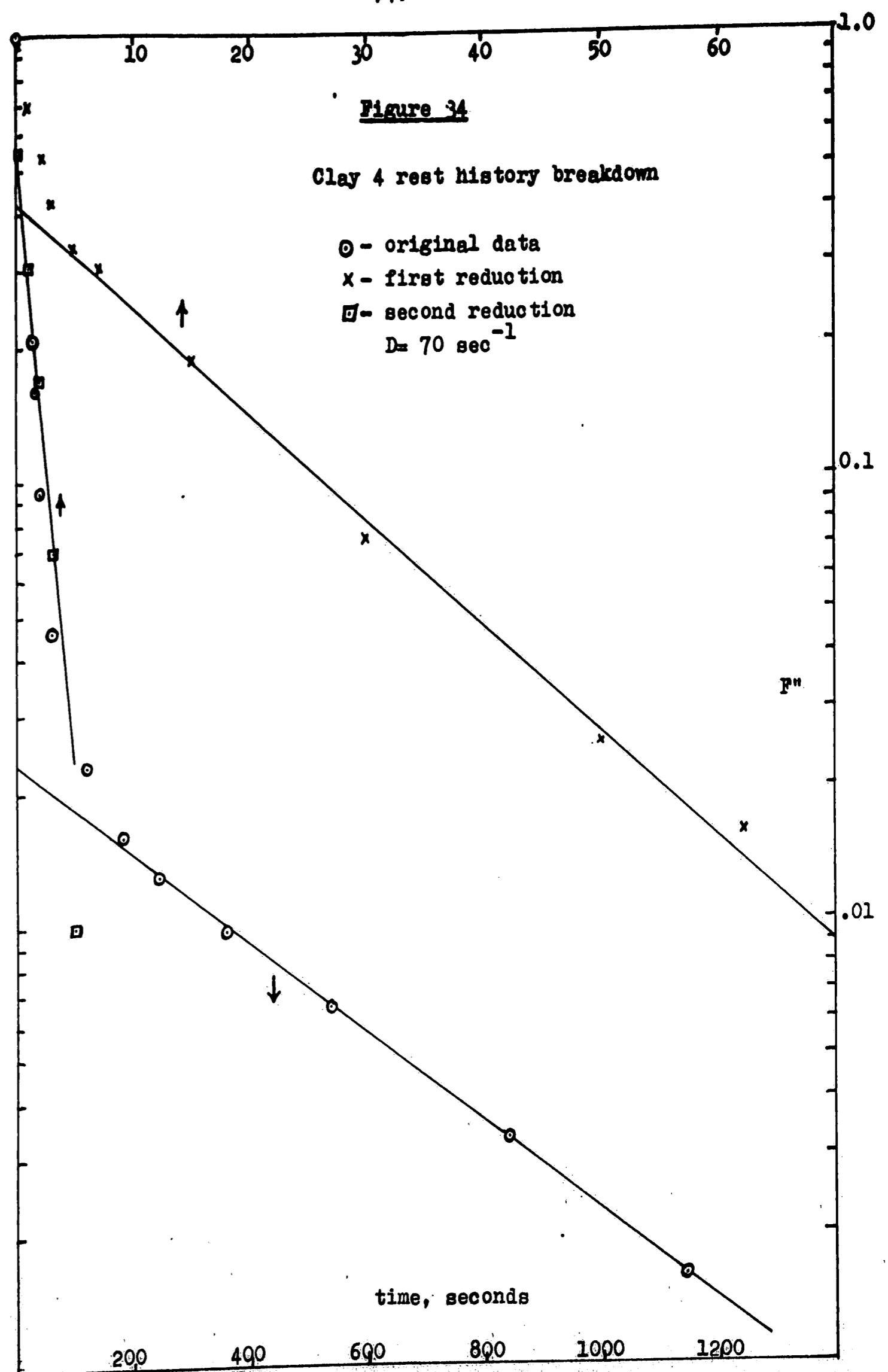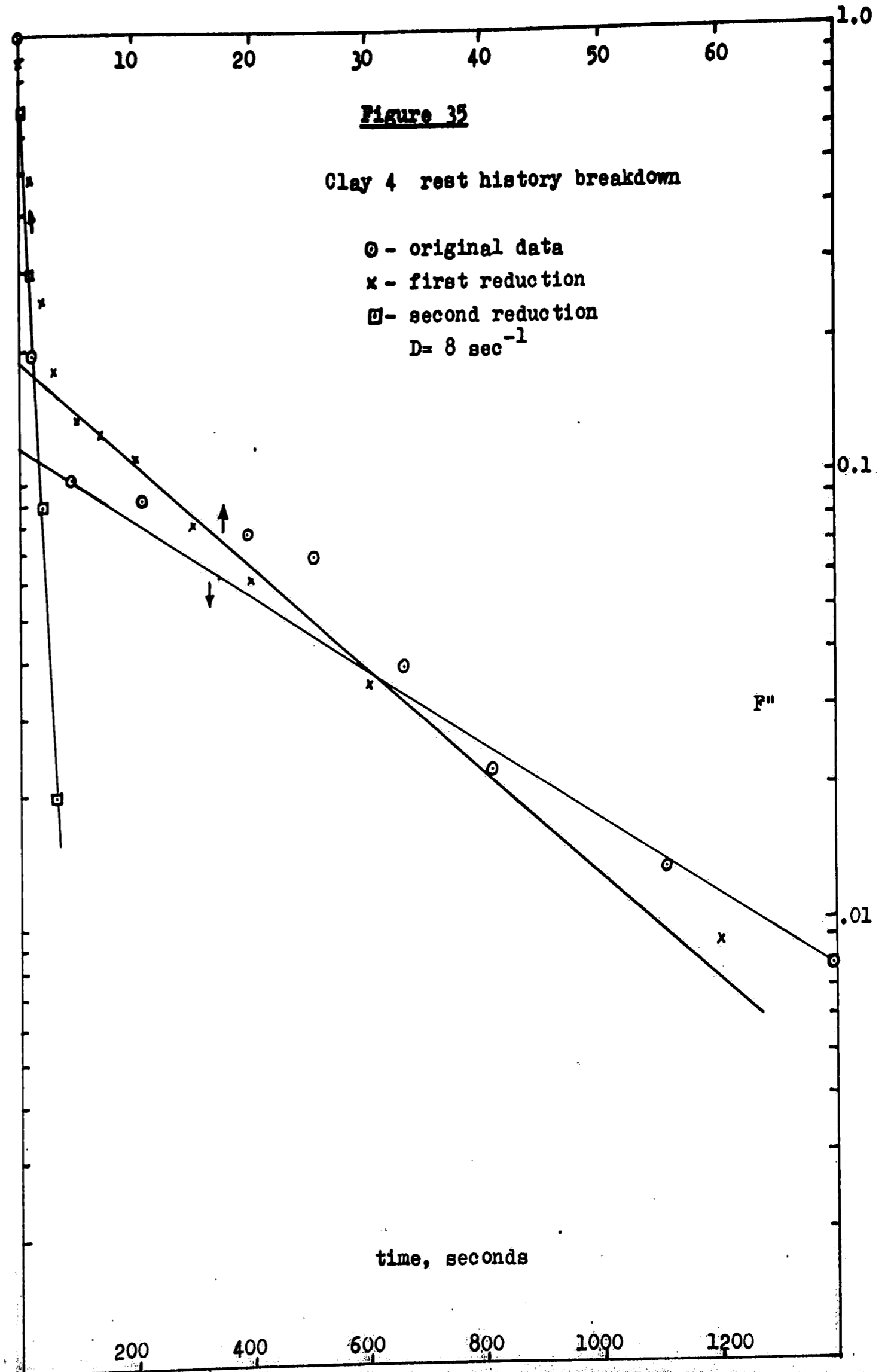**Figure 35**

Clay 4 rest history breakdown

⊙ - original data
x - first reduction
⊡ - second reduction
   $D = 8 \text{ sec}^{-1}$

F"

time, seconds

Figure 36

Clay 4 breakdown

⊙ – previous shear at 420 sec^{-1}
x – previous shear at 70 sec^{-1}
▼ – previous shear at 8 sec^{-1}

D= 1260 sec^{-1}

time, seconds

Figure 37

Clay 4 breakdown

⊙ - previous shear at 70 sec^{-1}
✗ - previous shear at 24 sec^{-1}
▣ - previous shear at 8 sec^{-1}
  D= 210 sec^{-1}
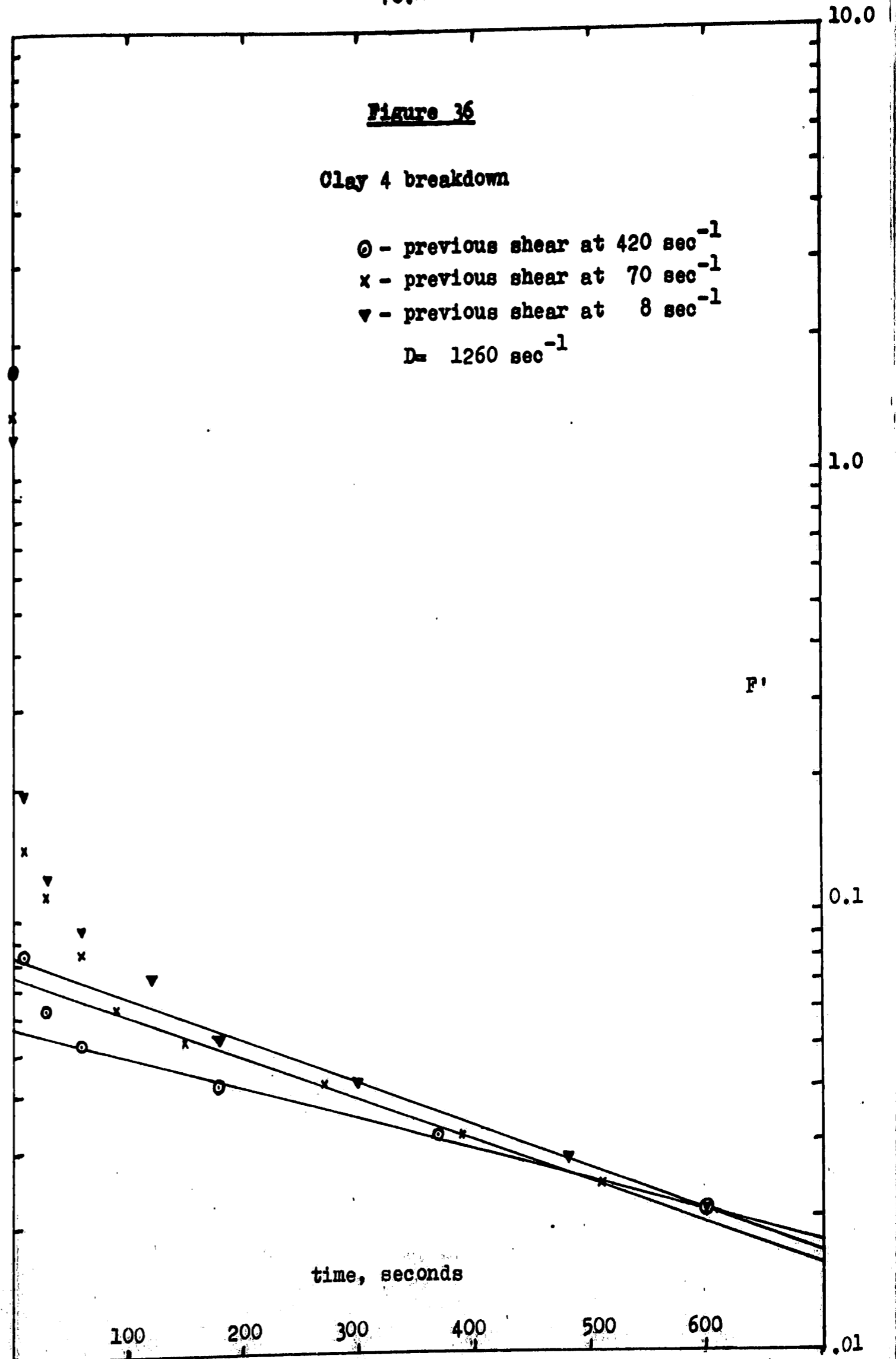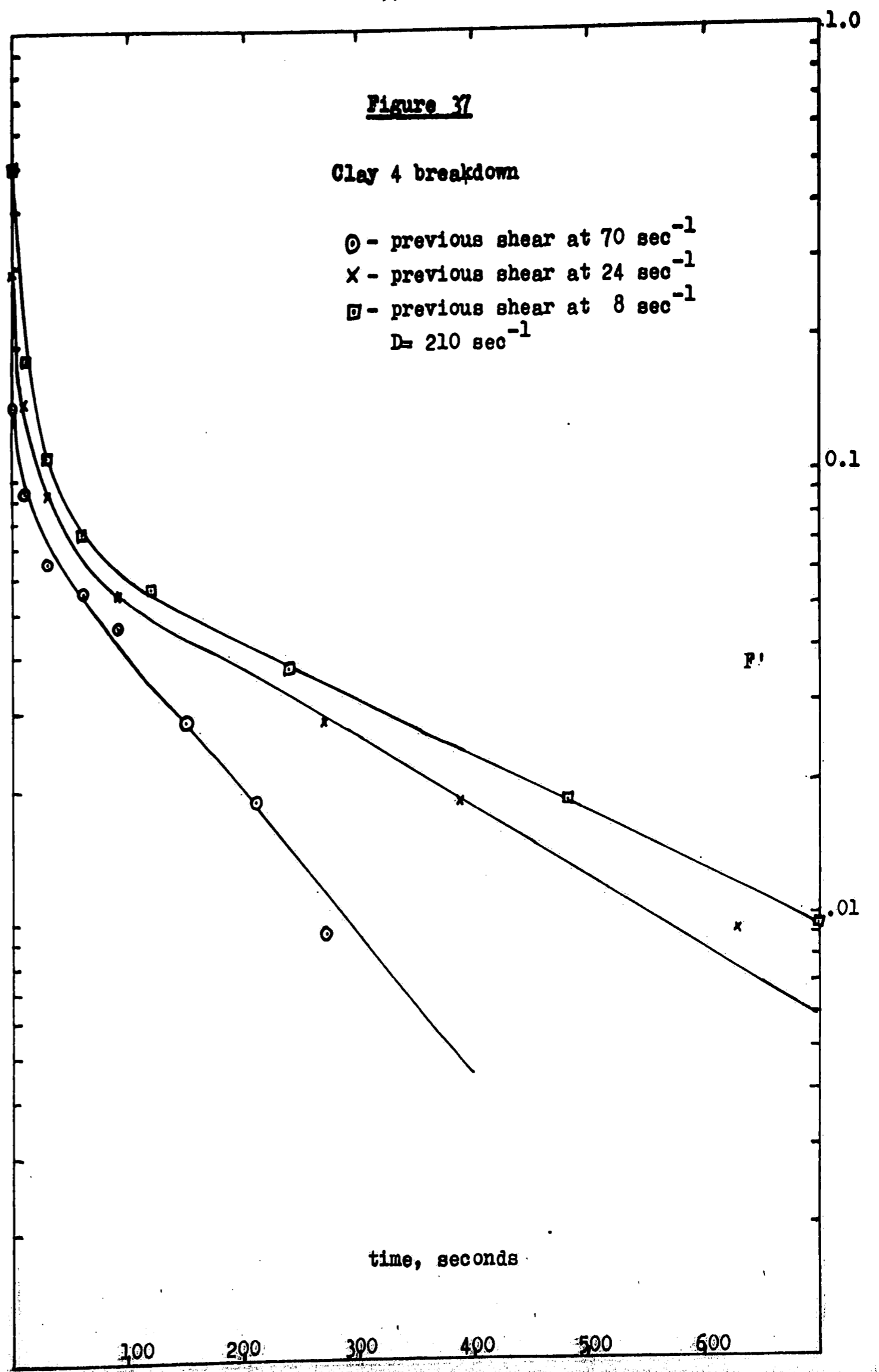
F'

1.0

0.1

.01

time, seconds

100   200   300   400   500   600

Figure 38

Clay 4 breakdown

- $\odot$ - previous shear at 24 sec^{-1}
- $\times$ - previous shear at 8 sec^{-1}
  - D= 70 sec^{-1}

time, seconds
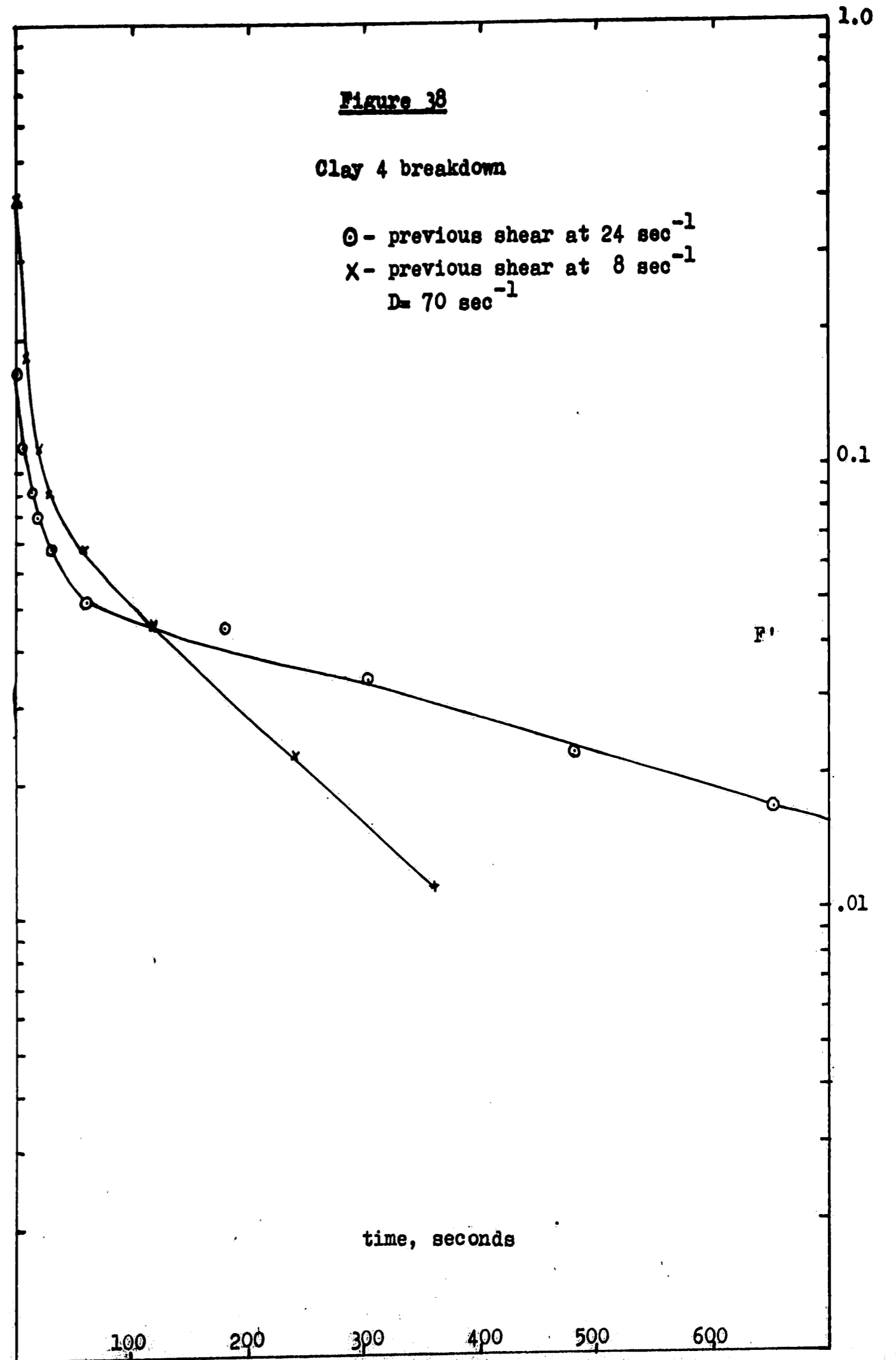
Figure 39

Clay 4 buildup

⊙ - original data
x - first reduction
previous ss @ 1260 sec^{-1}

D= 630 sec^{-1}

time, seconds
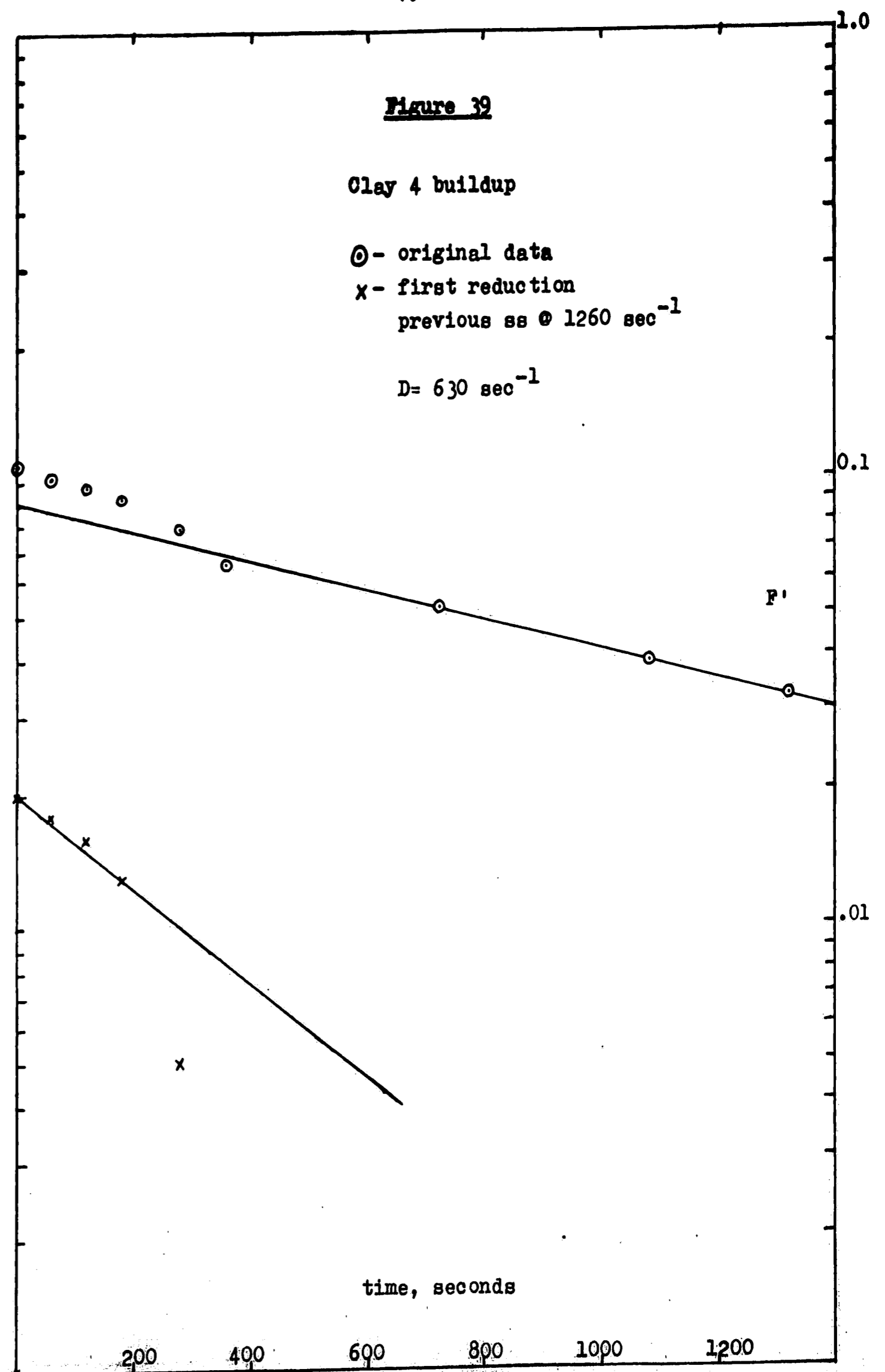
Figure 40

Clay 4 buildup

⊙ - original data
x - first reduction
   previous ss @ 1260 sec^{-1}

D= 8 sec^{-1}

F'

time, seconds
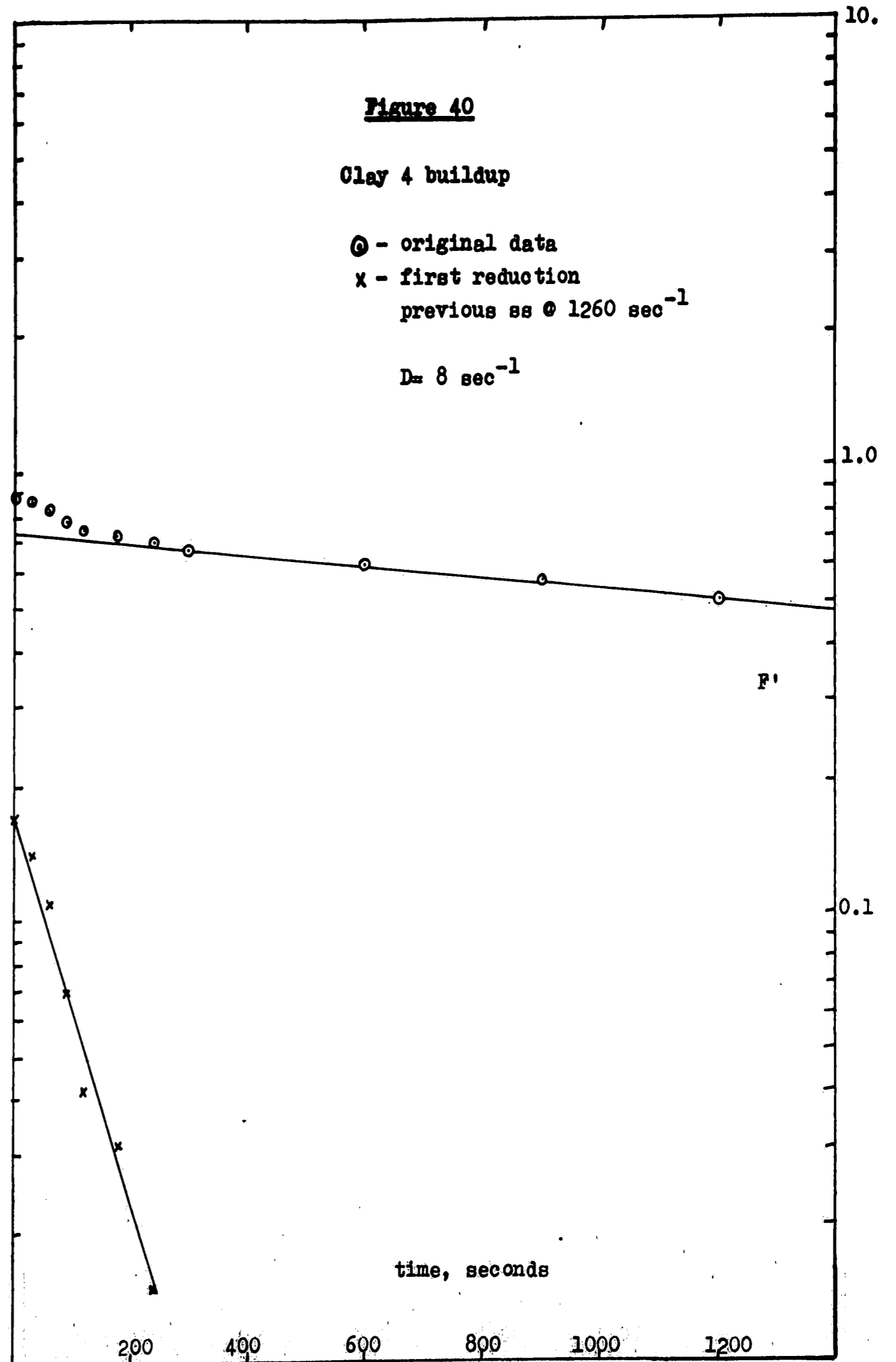
Figure 41

Clay 4 buildup

⊙ - previous ss @ 1260 sec^{-1}

⊗ - previous ss @ 630 sec^{-1}

D= 420 sec^{-1}

time, seconds
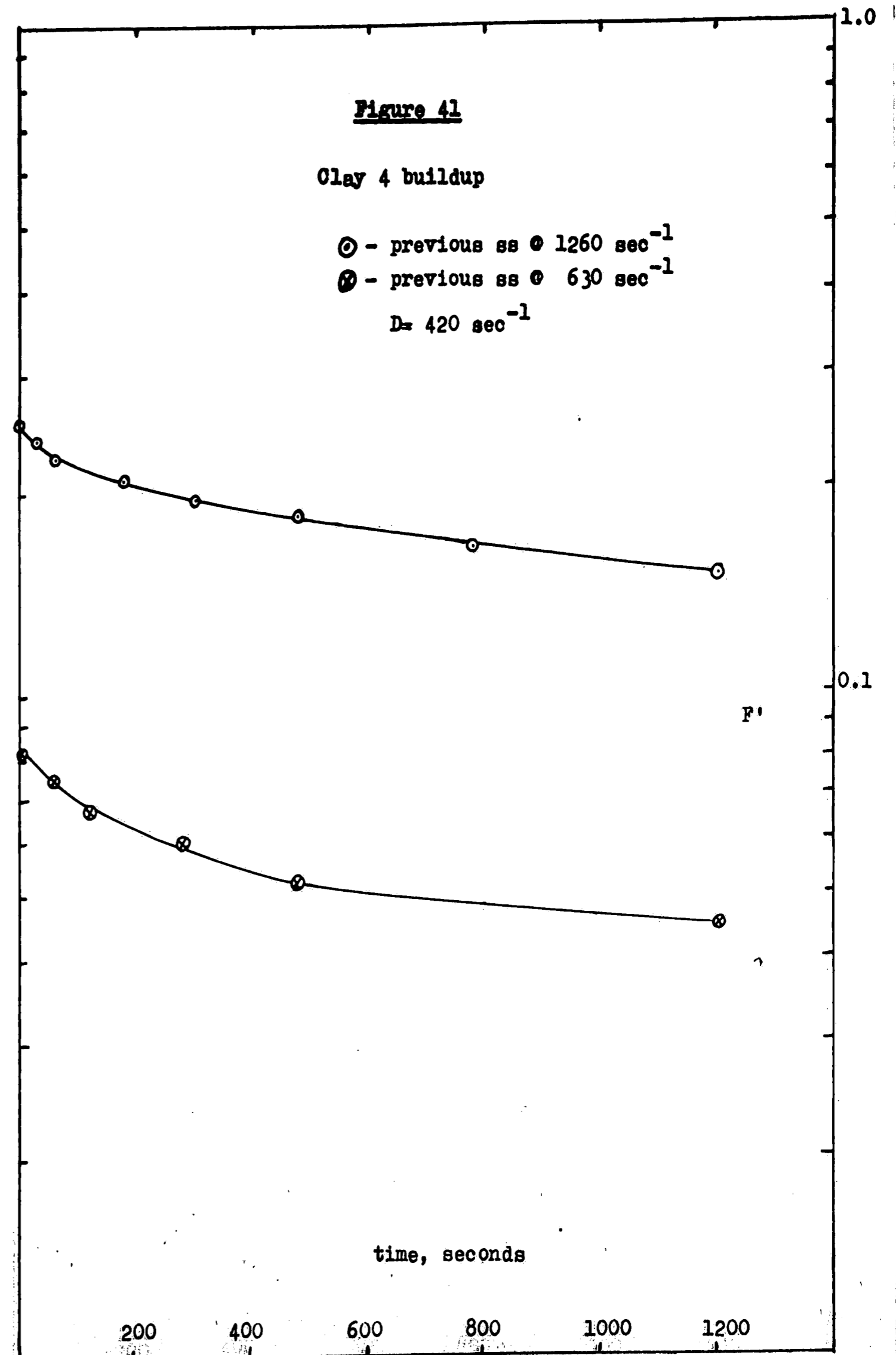
Figure 42

Clay 4 buildup

⊗ – previous ss @ 630 sec^{-1}
⊡ – previous ss @ 420 sec^{-1}
   D= 210 sec^{-1}

F'

1.0

0.1

time, seconds

200   400   600   800   1000   1200
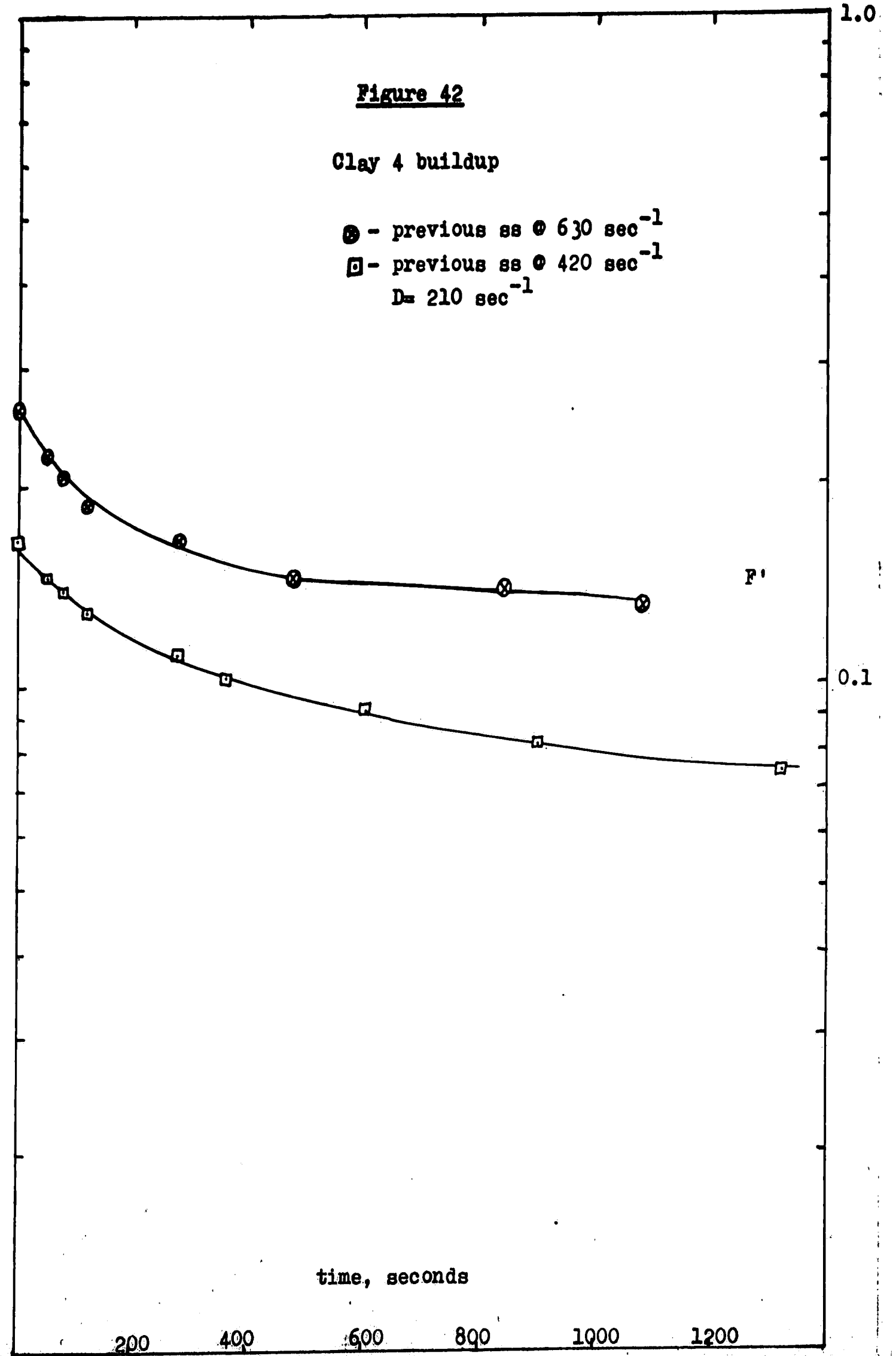
Calculations

1. Procedure X

From the data of Clay 4 (breakdown from rest at
$420 \ sec^{-1}$, Figure 32), the straight line at long times
has an intercept of $k_2 = .023$ and a slope, m_2, of
$(\ln .023 - \ln .0092)/-400$ sec. Simple graphical subtraction,
$F''(curve) - F''(straight line)$, is employed to get the
second curve, which is the 0- 70 second time response
signified by the "x"'s on the plot (Fig. 32). Approxi-
mating the longer time behavior with a straight line
gives an intercept of $k_1 = .074$ and a slope, m_1, of
$(\ln .074 - \ln .050)/-10$ sec. Further graphical subtraction
yields the points enclosed in boxes. An approximate
straight line is drawn through these points to give an
intercept of $k_0 = .903$ and a slope, m_0, of $(\ln .903 -
\ln .210)/-5$ sec. The values for the slopes and inter-
cepts are tabulated in the Results section of this
work (Table II).

2. Comparison of Procedure X fit with actual experimental data

For Clay 4 at 1260 sec^{-1} (Figure 6), we have the following data:

@ t= 20 sec, F"= .125

@ t= 60 sec, F"= .086

@ t=720 sec, F"= .016

The Procedure X fit reads, F"= $k_0 exp(-m_0 t) + k_1 exp(-m_1 t) + k_2 exp(-m_2 t)$. The constants from Table II are

k_0= .841 m_0= .49946

k_1= .082 m_1= .02473

k_2= .077 m_2= .00209

@ t= 20 seconds:

F"= .841exp(-.49946x 20) + .082exp(-.02473x 20) + .077exp(-.00209x 20).

F"= .841 exp(-9.9892) + .082 exp(-.8946) + .077 exp(-.0418)

= .841 x .000046 + .082 x .408777 + .077 x .95251

= .00003867 + .0335197 + .073343

F"= .1069

@ t= 60 seconds:

F"= .841exp(-.49946x 60) + .082exp(-.02473x 60) + .077exp(-.00209x 60)

F"= .841 exp(-29.9676) + .082 exp(-1.4838) + .077 exp(-.1254)

= .841 x 0 + .082 x .226778 + .077 x .883390

= 0 + .01859579 + .06803103

F"= .0866

@ t= 720 seconds:

F"= .841exp(-.49946x 720) + .082exp(-.02473x 720) + .077exp(-.00209x 720)

F"= 0 + 0 + .077 exp(-1.5048)

= .077 x .22202

F"= .0171

3. Temperature Effects

a) From the Instruction Manual 105 (13), page 19, the temperature effects due to viscous heating are negligible when using the MV I Couette system at $20.0^\circ C$.

b) Poehlein's analysis (28) gives a temperature correction factor for Newtonian fluids in a Couette viscometer. The correction factor can be applied to the non- Newtonian case as a rough approximation. Figure 43 shows the variation in normalized viscosity as a function of β, a dimensionless group.

$$\beta = a\ \delta^2 \tau^2 / 4 \eta_0 k$$

where,

a= viscosity- temperature coefficient for fluids that obey $\eta/\eta_0 = \exp(-a(T- T_0))$. For water, data in reference (9) are as follows:

T, $^\circ$C	η, cp
20	1.005
25	.894
40	.656

therefore, <u>a= .022 $^\circ C^{-1}$</u>

k= thermal conductivity, for water this is (9), 1.44×10^{-3} cal/ sec-cm-$^\circ$C
$= 1.44 \times 10^4$ g-cm^2/sec^2-sec-cm-$^\circ$C, given that 1 cal= 10^7 ergs= 10^7 dyne-cm= 10^7 g-cm^2/sec^2

δ = gap width between cup and bob, for MV I system this is <u>= .25 cm</u>

τ = shear stress developed (at highest shear rate). For Clay 4 about <u>300 dynes/cm^2</u> were developed at 1260 sec^{-1} for a considerable amount of time.

$$\eta_o = \tau/\dot{\gamma} = 300/1260 = .25 \text{ g/cm-sec for Clay 4}$$

$$\beta = \frac{(.022)^oC^{-1} \ (.0625)cm^2 \ (9.0x \ 10^4) \ g^2/cm^2\text{-sec}^4}{4(.25) \ g/cm\text{-sec} \ (1.44x \ 10^4) \ g\text{-cm/sec}^3\text{-}^oC}$$

$$= .0086$$

Figure 43 shows no viscous heating effects for water based solutions at this value of β. All fluids tested contained water as the major component. For shear stresses ten times greater viscous heating is still not a major problem.

Figure 43

-87.-
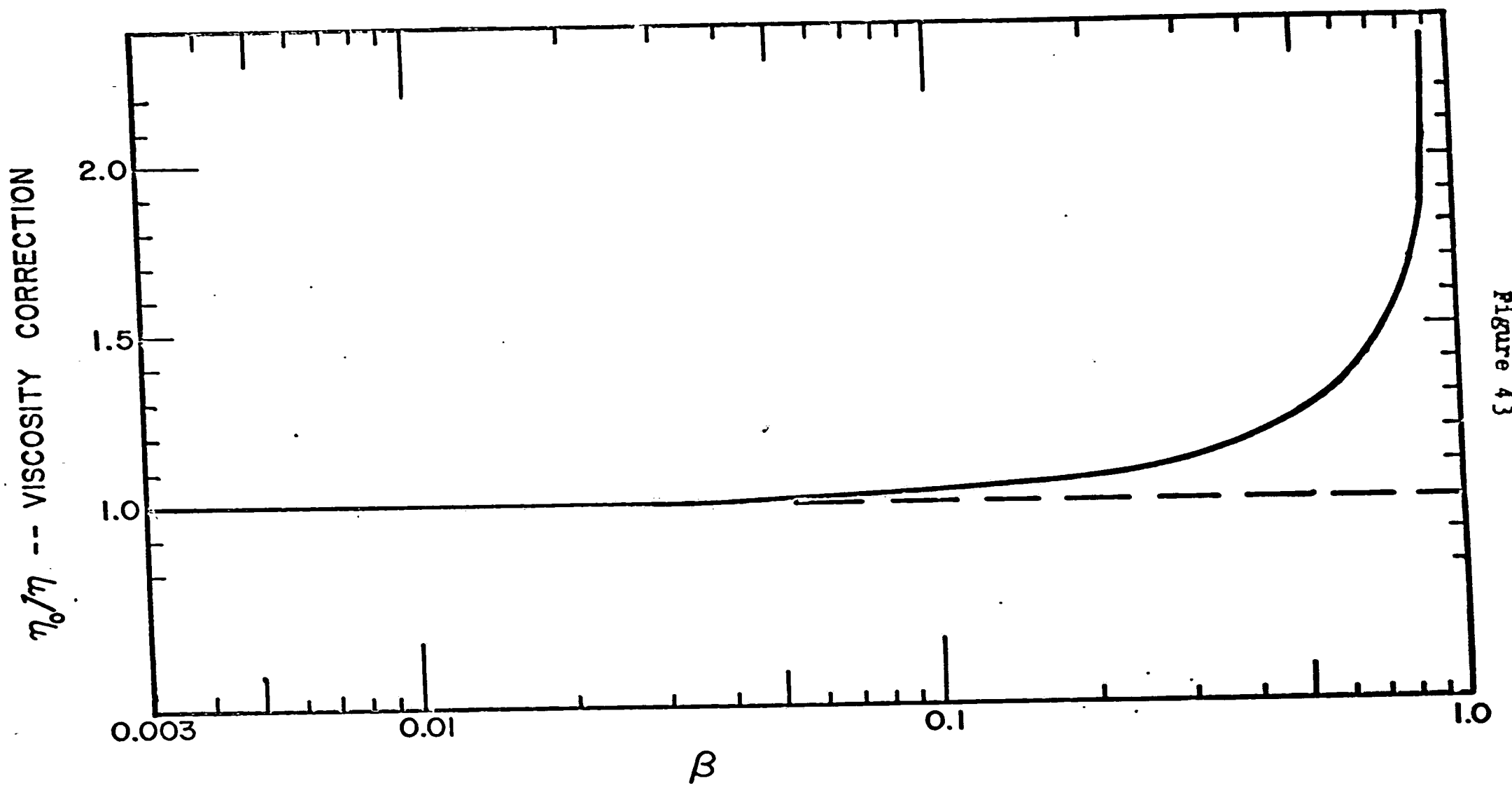
-- COUETTE VISCOMETER TEMPERATURE
CORRECTION

4. Conversion Factors

Using a calibrating oil and the procedure described in the operating manual (13), the "K" values for a particular rotor were determined. These values were corroborated by J.C. Kelsall, Lafayette College '69.

"K" values for the rotors:

rotor	"K" value	"f" value	A= "K" x B
MV I	2.30	6.55	29.0×10^2
MV II	6.93	7.53	33.2×10^2
MV III	19.95	10.90	48.0×10^2

For measuring heads,

$$a_{500} = 4.4$$
$$a_{5000} = 50.2$$

$$B_I = a\ f\ 10^2 / "K"_I = 1260$$
$$B_{II} = \quad " \quad / "K"_{II} = 480$$
$$B_{III} = \quad " \quad / "K"_{III} = 240$$

$$D = B/U, \quad U = \text{gear number}$$
$$F = S"K"B \times 10^{-2}, \quad S = \text{stress reading in millivolts}$$
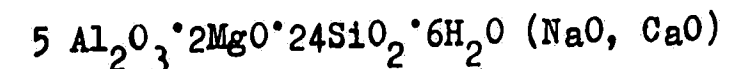
Material Specifications

1. **Mayonnaise** - Hellmann's Real Mayonnaise commercially available at the local A & P.

2. **Paint** - "Dripless Vinyl Wall Paint" (Rubberite), a commercial sample obtained at the local hardware store. The paint was manufactured by the Monad Paint and Varnish Company, Philadelphia 23, Pennsylvania. The paint bore No. 62221512, and its composition was as follows: (by weight) TiO_2 (9.3%), $CaCO_3$ (13.7%), silicates (17.8%), vinyl-acrylic polymer (12.7%), water (46.5%).
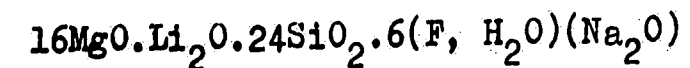
3. **Cmc** - The cmc was DuPont carboxymethyl cellulose P-75-H, Lot 2068 (11/21/66). It was mixed with water according to the following table:

wt%cmc	g, cmc	g, H$_2$O	g, cmc/g, total
1.0	1.01	100.0	1.01/101.01
1.5	1.55	100.0	1.55/101.55

4. **Clay 4** - 650-135 from an undisclosed source. This clay is a synthetic inorganic Hectorite. Hectorite is related structurally to Montmorillonite and belongs to the Montmorillonite group (20). Montmorillonite is the essential mineral in bentonite rock.
   Montmorillonite:
   $$5 Al_2O_3 \cdot 2MgO \cdot 24SiO_2 \cdot 6H_2O \ (NaO, CaO)$$
   Hectorite:
   $$16MgO.Li_2O.24SiO_2.6(F, H_2O)(Na_2O)$$

Equipment Specifications

1. Rotovisco - Brinkman Instruments Company, 115 Cutter
   Mill Road, Great Neck, L.I., N.Y. Model
   number 62010. System MV I used with 500
   head and constant temperature bath assembly.

2. Recorder - variable voltage (0-1,2,5,10,20,50,... milli-
   volts) variable chart speed recorder.
   Moseley Autograf, Model 7100B strip chart
   recorder from Moseley Division - Hewlett
   Packard, 433 North Fair Oaks Avenue,
   Pasadena, California.

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X. VITA

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The author obtained his elementary school education from the New York City Public School System in Queens. In 1963 he completed his secondary school education at W.C. Mepham High School in Bellmore, Long Island. The author received his Bachelor of Science in Engineering from Princeton University in 1967. He is a student member of the American Institute of Chemical Engineers and an Associate member of the Society of the Sigma Xi. His first contribution to the body of science resulted from the bachelor thesis work and has been published in Analytical Chemistry 40(6), 876 (1968).

Practical experience in the form of industrial employment was obtained at Dynamit Nobel, A.G., Troisdorf, West Germany for the summer of 1965 and at Hercules, Inc., Parlin, New Jersey and Wilmington, Delaware for the summers of 1966 and 1968, respectively.

The author is presently engaged to Miss Claudia E. Tindall of Trenton, New Jersey and will be married in June, 1969. His present plans are to continue graduate studies at Lehigh University upon completion of the necessary requirements.