AN INVESTIGATION TO DETERMINE A SUITABLE CONTROL PROCEDURE FOR THE CONSISTENCY OF AN OIL-IN-WATER OINTMENT BASE, USING A ROTATIONAL VISCOMETER

By

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A Thesis submitted in Partial Fulfillment
of the requirements for
the Degree of
MASTER OF SCIENCE
(Pharmacy)
at the
UNIVERSITY OF WISCONSIN

1952

ACKNOWLEDGMENT

The author wishes to express his thanks to Professor L.W.Busse who guided the work, and to the Directors of The Interchemical Corporation of New York for the opportunity provided him to work in the rheology laboratory under the guidance of Mr.S.Krakauer. He also wishes to thank Mr. R.Bulas of that laboratory for a confirmation of the work with the Interchemical Rotational Viscometer.

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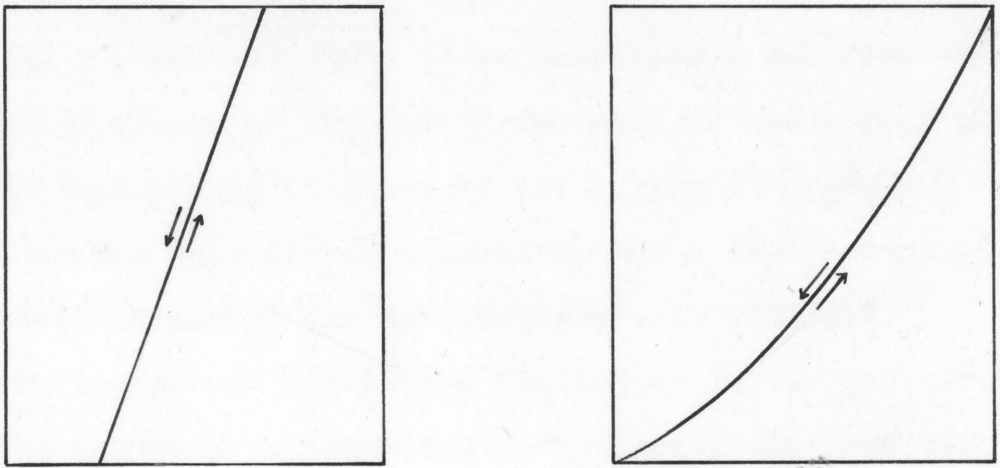
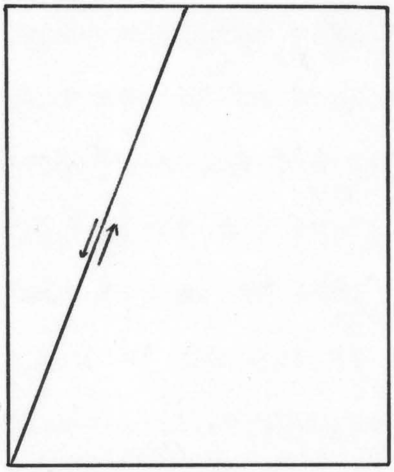
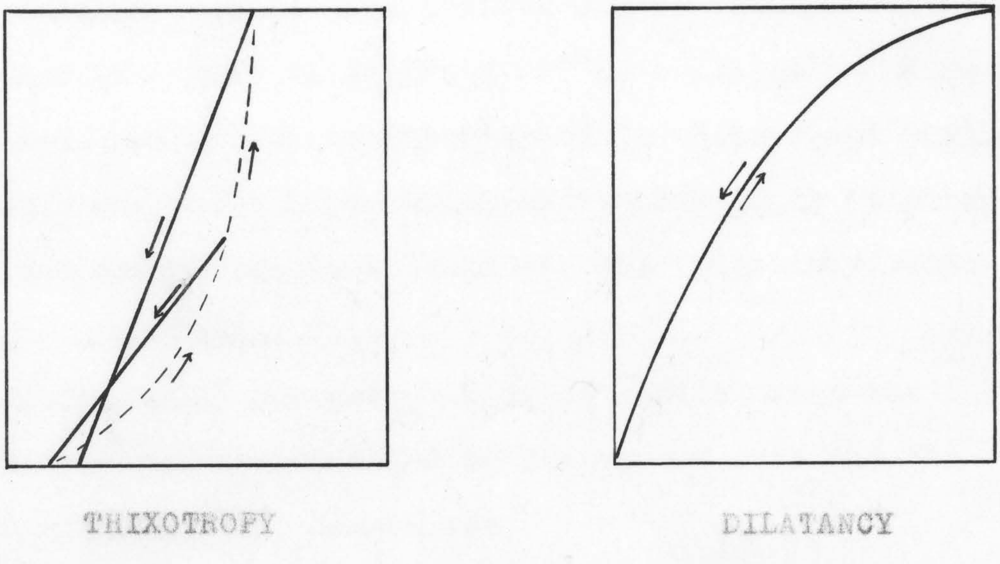


PLASTICITY PSEUDOPLASTICITY



NEWTONIAN FLOW



THIXOTROPY DILATANCY

Figure 1.
(r.p.m. against torque)

INTRODUCTION

Many preparations used and prepared by the pharmacist are of a semi-solid consistency.* Emulsions, extracts, gels, ointments and suspensions and the preparations from such naturally-occurring substances as acacia, agar, bentonite, gelatin and tragacanth, cover a wide field for consistency control. With the exception of petrolatum (petroleum jelly), no standards of consistency have been adopted for these semi-solid substances. In the case of ointments, the vaguest indication that consistency is important and may be controlled is given in the U.S.P. XIV: 'In official ointments which contain petrolatum, white petrolatum, yellow wax, or white wax, the proportions of these may be varied to maintain a suitable consistence under the different climatic conditions, ...'

When we wish to measure the consistency of liquid petrolatum, for example, no difficulty is encountered, for we find that its flow can be explained by Newton's law of flow, and its consistency can be expressed by a coefficient, the coefficient of viscosity, often referred to simply as viscosity. The preparations previously mentioned, however, are some of a large group of substances which show deviations from Newton's law of flow. They are known as non-Newtonian

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*Consistency - That property of a body by virtue of which it tends to resist deformation. (A.S.T.M. E.24-42) substances, and are said to exhibit anomalous viscosity. A search of the literature reveals many conflicting views on the methods for determining their consistency, and we find that investigators in various industries have designed methods of measurement specifically for each product. Most of the methods seem to be too empirical and are inadequate from the standpoint of reproducibility.

EMPIRICAL METHODS OF CONSISTENCY CONTROL

A. Penetrometers

Penetrometers which have been made in many forms: rods, spheres, discs and plates and from various substances, can be divided into two main groups:

I. The plunger moves under its own weight into the substance under test.

(a) A constant weight penetrometer

The pentrometer recognized by the U.S.P.XIV for testing the consistency of petrolatum, is that of the A.S.T.M. specification. (1)(2) It was developed by the petroleum industry for a wider range of consistency control and is not completely satisfactory for pharmaceutical petrolatums. The instrument measures, in tenths of millimeters, the distance that a metal cone of standard weight and shape will penetrate into the material in 5 seconds, when released exactly at the surface.

(b) A variable weight penetrometer

To measure the strength of gelatin gels, the Bloom gelometer is used. The effective weight of the cylindrical ebonite plunger is increased at a constant rate by allowing lead shot to run into a funnel attached to the penetrometer. The weight necessary to produce a given depth of penetration in a given time is used as a measure of the consistency. (3)

II. The substance under test moves at a constant rate against a stationary plunger.

(a) A constant rate penetrometer

The constant rate penetrometer developed by the British Building Research Station, uses a moving platform and a fixed needle-like penetrometer. The head of the penetrometer needle is fixed to a spring carrying a mirror from which a beam of light is directed onto a scale, so that the variation in the penetration may be recorded.

Many modifications in the method of use have been advocated: some instruments are placed on the surface of the substance under test as in the U.S.P. penetrometer, others are dropped from a given height and still others start below the surface of the product. An instrument of the latter type using a disc has been described by Fiero in attempting to correlate the consistency of various hydrogenated fats and oils with the softening point. A metal disc 1.6 cm. in diameter is attached to a vertical rod and pan upon which weights can be placed. A scale attached to the rod indicates the extent of penetration. (4)

B. The line spread consistometer

This test measures the increase in area which takes place after a given length of time when a given mass of the material, shaped in the form of a cone or cylinder, is allowed to deform. The material is placed in the center of a plate which bears a number of equally spaced concentric rings and the spread which occurs is a measure of the consistency. (5)

In a modification of the line spread consistometer test, the slump test, the plate is allowed to fall through a given height at regular time intervals. (6)

C. The parallel plate test

A modification of the above test uses two parallel plates between which the material spreads. This method was applied to incendiary gels; the diameter in centimeters to which 5 c.c. of the gel will spread in one minute, between two parallel plates under a load of 2000 G., was used as a measure for the comparison of consistency. It was found that when the diameter of the gel after spreading was plotted against the logarithm of the time for which the load was applied straight lines were obtained. (5)(7)(8)

All of the above methods have been criticized for the same reason, viz. they only give a measure of the consistency at that particular rate of shear and no indication whatsoever of the viscosity at a lower or at a higher rate of shear. They are known as one-point methods. It is argued, however, in their defense, that for the same preparation they do offer some measure of standardization.

CONSISTENCY CURVE METHODS

In an attempt to obtain a better knowledge of consistency, many instruments have been developed to obtain consistency curves. It has been shown that the observed viscosity of many products decreases with increasing rate of shear, and approaches a constant value at high shear. This limiting value of the system has been used by a number of workers to derive expressions for the consistency of dispersed systems viz. suspensions and emulsions. (9)(10) The limiting viscosity, though a criterion of the system, is little better than a one point method in many cases. Other advantages of the consistency curve methods are:

1. A graph can be drawn of the consistency obtained at different rates of shear to indicate the complete behavior and the presence of yield value.
2. The change of consistency with time at one particular rate of shear. (The limiting viscosity is just the final minimum value obtained.)
3. The increase of consistency with time after shearing.

The two main groups of instruments by which consistency curves can be obtained are:

A. <u>Mobilometers</u>

The mobilometer consists of a cylinder to contain the sample and a circular performated disc or cone which is attached to a stem, thus permitting the disc to descend evenly and providing a means of measuring its descent. The rate of fall of the disc, or the rate of shear, can be altered by placing a suitable weight on the pan at the upper end of the disc stem. The instrument was first described by Gardner and Parks (11) for the control of the flow properties of paints, enamels and lacquers. Numerous other workers have applied the method to both Newtonian and non-Newtonian preparations. Thus Gardner and Van Heuckeroth (12) have used it for food products, mineral oils, petrolatum and coal tar; Gray and Southwick (13) for mayonnaise; Turnbull (14) and McIntyre & Urwin (15) for clay slips; Baldeschweiler and Wilcox (16) for viscous mineral oils and Kinney (17) for adhesives and various soft plastics.

B. Rotational Viscometers

There is no complete agreement among the various schools of thought on the interpretation of the consistency curves obtained from rotational viscometers. A brief consideration of three approaches to the interpretation of these curves is outlined below.

1. The Goodeve school which considers that a quantitative measurement of the viscosity of a non-Newtonian substance can be made and can be expressed in poise. When the apparent viscosity i.e. the ratio of the shearing force to the rate of shear is plotted against

the reciprocal of the rate of shear, the slope of the line is the coefficient of thixotropy and the intercept on the viscosity axis the limiting viscosity of the system. (18) Goodeve and Whitfield in referring to a thixotropic system state:

> "As the rate of shear increases the viscosity decreases. Usually the change is reversible - either quickly or slowly. If such a liquid is subjected to a continuous and uniform shear a steady state may be set up, the viscosity coefficient for which may be accurately measured. ... this steady state corresponds to an equilibrium between the process by which an internal structure is built up and the breaking down process arising from the shear." (19)

2. The Bingham-Reiner-Green adherents, who divide non-Newtonian behavior of substances into three groups:

   (a) Pseudoplasticity

   A substance shows pseudoplasticity when a consistency curve starts at the origin and shows a decrease in viscosity with increased rate of shear. The full curve is necessary to characterize the substance.

   (b) Plasticity (a Bingham body)

   A substance which has a definite yield value expressed in dynes per sq.cm., and a 'plastic viscosity', measured in poise. Does not start at origin.

   (c) Dilatancy

   A substance which shows an increase in viscosity with increased rate of shear, exhibits dilatancy. The full curve is necessary to characterize the substance.

For a substance which shows thixotropy, the area under the curve obtained by increasing the rate of shear to a given value and decreasing it again to its original value is a measure of the thixotropic breakdown, and a coefficient of thixotropic breakdown can be calculated. (20)(21)(22)

The Interchemical rotational viscometer is the instrument developed by Green to illustrate practically the theories advanced by Bingham and mathematically formulated by Reiner and Rivlin. (23)(24)

The consistency curve obtained with the Interchemical rotational viscometer consists of an upcurve and a downcurve. The upcurve is obtained by plotting the deflection obtained at each point when the r.p.m. of the cup is increased stepwise. At a chosen maximum r.p.m. of 100, the deflection is again recorded as the speed of the cup is decreased at the same interval as the upcurve. The changes are made without stopping the rotation of the cup and are spaced as evenly as possible both in regard to r.p.m. and time. A schematic representation of some curves which can be obtained with this instrument are shown in figure 1 . The calculation of results is accomplished by the application of the Reiner and Rivlin equation. For a substance which shows plasticity (a Bingham body), two values can be calculated, the 'plastic viscosity' U and the yield value f.

The 'plastic viscosity' U is determined from the cotangent of the angle formed by the torque axis and the linear portion of the downcurve:

$$U = \frac{(T - T_2).S}{\omega}$$

where T is the torque, T_2 the intercept, ω the angular velocity, and S one of the two instrumental constants.

$$S = \frac{\frac{1}{(R_b)^2} - \frac{1}{(R_c)^2}}{4.\ \pi\ .h.}$$

where R_c is the radius of the cup, R_b the radius of the bob, and h the corrected height of the bob.

The yield value f in dynes per sq.cm. is obtained by multiplying the torque intercept T_2 by the second constant C.

Thus $f = C.T_2$

where $C = \frac{S}{\ln \frac{R_c}{R_b}}$

The values to convert the slope of the line to the 'plastic viscosity' U and the intercept T_2 to the yield value f for the instrument used are respectively 0.263 and 19.4.

3. The Pryce-Jones school, which considers that it is necessary to make at least two curves to indicate the consistency of a non-Newtonian substance. It is inferred that the results are only of a semi-quantitative nature. The term poise should be used only for Newtonian substances. Differences between Newtonian, dilatant, plastic and thixotropic behavior can be established, but the coefficient of viscosity of the Goodeve school and the coefficient of thixotropic

breakdown of the Green school and quantitative expressions of 'plastic viscosity', yield value and limiting viscosity are valueless. (25)(26)(27)

The method used by Pryce-Jones is described in his 1936 paper:

> 'In principle the apparatus consists of a torsion viscometer in which a cylinder, suspended from a torsion wire, is immersed in the thixotropic fluid. The cylinder is deflected from zero to an angle of 25°, and on being released gradually returns towards zero with an angular velocity which is inversely proportional to the viscosity of the fluid. ... The shearing force at any point on the curve is proportional to the deflection A and the rate of shear is proportional to the slope of the curve, or tan θ where θ is the angle the tangent to the curve makes with the time axis. The viscosity at any point on the curve is, therefore, K.A / tan θ. In a true liquid the viscosity is independent of the rate of shear, and, therefore A/tan θ is a constant and the time / deflection curve is, therefore, logarithmic. ... The curve for a true liquid is independent of the time that has elapsed after the liquid has been stirred, and co-incident curves are obtained however long the cylinder is left at rest in the deflected position. In a thixotropic fluid different curves are obtained for different resting periods after stirring has ceased.' (26)

The time deflection curves which are not logarithmic, i.e. where the consistency is a function of the rate of shear, can be divided into two groups:

A. If the curves taken at different intervals after shearing are coincident, the system can be said to exhibit anomalous viscosity.

$$\underset{\eta_1}{\text{Fluid}} \quad \xrightleftharpoons[\text{end of shear}]{\text{shear}} \quad \underset{\eta_2}{\text{Fluid}}$$

where $\eta_1 > \eta_2$

Viscosity is a function of rate of shear alone.

B. If the curves are not coincident, then the consistency is both a function of the rate of shear and the past history of the system. The system is said to exhibit thixotropy. Substances showing this latter phenomenon were further subdivided into two classes depending upon the rate of increase in consistency after shearing.

1. False-body thixotropy

The increase is marked in the first few minutes of rest and the build-up becomes progressively smaller with the passage of time. (See fig. 2)

$$\underset{\eta_1}{\text{Gel}} \overset{\text{shear}}{\underset{\text{rest}}{\rightleftharpoons}} \underset{\eta_2}{\text{Gel}}$$

where $\eta_1 > \eta_2$

Viscosity is a function of rate of shear and of time.

2. Thixotropy

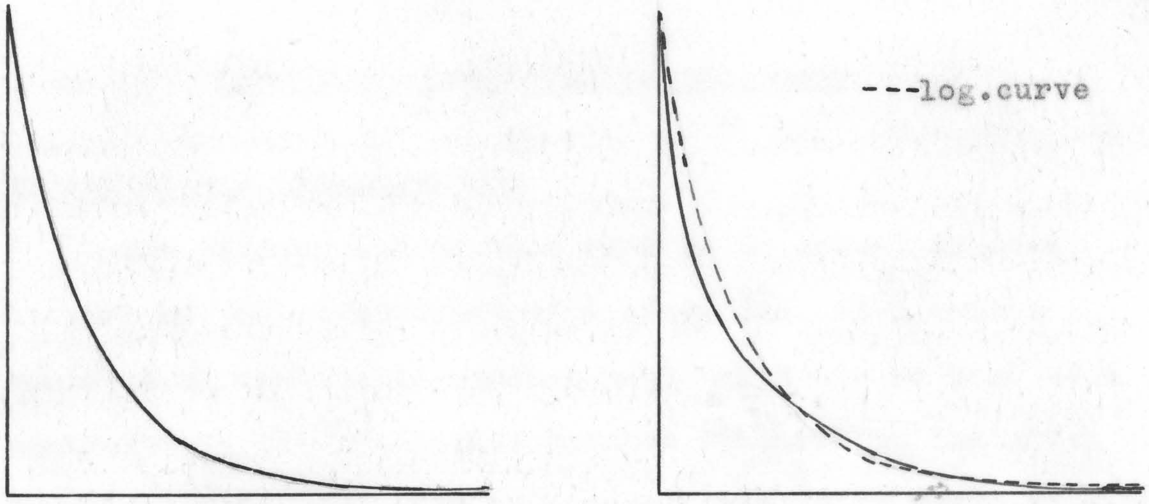
The initial increase is small and the rate of increase in consistency is more gradual than that of false-body thixotropy. It is considered to be more closely approximate to the 'true' thixotropy originally described by Freundlich. (See fig. 2)

$$\underset{\eta_1}{\text{Gel}} \overset{\text{shear}}{\underset{\text{rest}}{\rightleftharpoons}} \underset{\eta_2}{\text{Sol}} \overset{\text{rest}}{\underset{\text{shear}}{\rightleftharpoons}} \underset{\eta_1}{\text{Gel}}$$

where $\eta_1 > \eta_2$

The sol will exhibit Newtonian viscosity.

Viscosity is a function of rate of shear and of time.

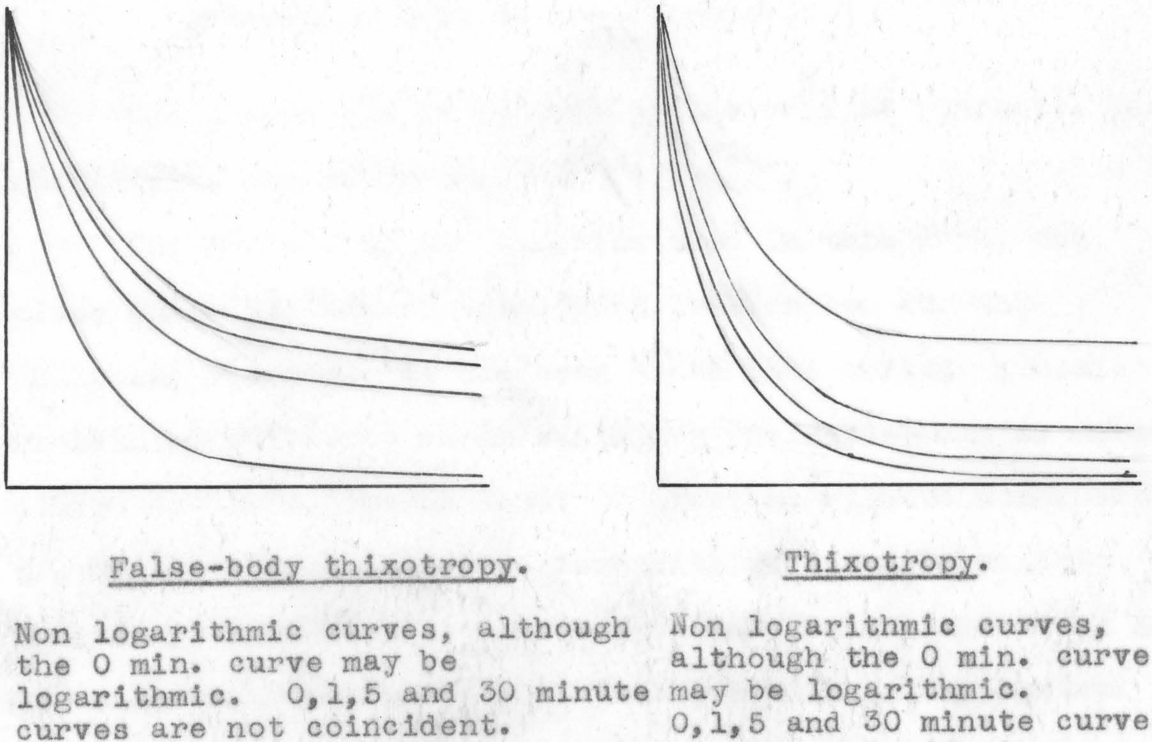


Newtonian Flow.

a logarithmic curve showing
0,1,5 and 30 minute curves
coincident.

Anomalous Viscosity or
Non Newtonian Flow

a non logarithmic curve showing
0,1,5 and 30 minute curves
coincident.



False-body thixotropy.

Non logarithmic curves, although
the 0 min. curve may be
logarithmic. 0,1,5 and 30 minute
curves are not coincident.

Thixotropy.

Non logarithmic curves,
although the 0 min. curve
may be logarithmic.
0,1,5 and 30 minute curves
are not coincident.

Fig. 2.
(deflection against time)

INTRODUCTION TO EXPERIMENTAL WORK

Object of the investigation

The primary aim of this work is to establish some measure of the consistency of a cream (an oil-in-water emulsion of semi-solid consistency) which can be used as a control test for production batches prepared to the given formula. This aim would be accomplished if it could be shown that:

1. The results from the same batch of cream are reproducible.
2. Batches of cream prepared to the same formula and method of preparation give the same results.
3. Deviations from the formula and differences in production methods are detectable.

The second aim is to examine the role of bentonite in stabilizing the emulsion.

The formula of the emulsion used in this work, and given under the experimental part, was chosen for the following reasons. It has been shown that certain emulsions containing bentonite as an auxiliary emulsifier can be autoclaved at 120°C. for at least 30 minutes, without separation of the oil phase. (28)(29) Bentonite is known to exhibit thixotropy (false-body thixotropy), and its incorporation in an emulsion might induce anomalous behavior in the system. It was therefore considered desirable to establish the procedure for the determination of the consistency of a bentonite-containing cream. This would probably entail greater difficulty than for a cream without bentonite, but it was thought any such procedure would be applicable, without modification, for the simpler systems of cream without bentonite. It was decided to confine the work initially to one speed of rotation of the cup, and since we are primarily concerned with low rates of shear, this was arbitrarily chosen as 12 r.p.m. The work was carried out at a temperature of 25°C. which was approximately that of the laboratory.

In the determination of the consistency, the bob of the viscometer should be immersed to the same level for each determination. For a cream of this consistency it was decided to use a given weight of cream, 100 G., which is more convenient than a volume measurement. This will be permissible for a given formula, allowing of course, a change in weight for changes in specific gravity of the materials used.

The instrument available for this work was a MacMichael viscometer, a readily available instrument of low cost. In common with many rotational viscometers, this instrument has a number of disadvantages some of which have been overcome in the more expensive apparatus:

1. The annular space between the cup and the bob is large, and the consistency of the preparation is such that the whole of the material is never sheared.

2. The distance between the bottom of the bob and the base of the cup is small, so that there will be a large end effect.

It is therefore not possible to express the rates of shear or the consistency in other than r.p.m. and MacMichael degrees respectively. Accordingly, therefore, the approach has been restricted to a comparative examination on a semi-quantitative basis.

I had however, the opportunity to work at The Interchemical Corporation, and a number of creams have been tested on a rotational viscometer designed by Green in which the rate of shear can be calculated and the viscosity expressed in absolute units.

EXPERIMENTAL

Creams containing bentonite

Preparation of cream

Cetyl alcohol	5.0
Liquid petrolatum	25.0
Sodium lauryl sulfate	0.5
Bentonite	2.0
Distilled Water	to 100.0

The liquid petrolatum and cetyl alcohol was heated to 60°C. A 5% bentonite suspension had been prepared and boiling water was added to bring to the correct weight at 60°C., when the sodium lauryl sulfate was added and dissolved.

The oil phase was added to the aqueous phase and the resulting emulsion was stirred and passed through a hand homogenizer, previously warmed. The emulsion was collected in an ointment jar, and shaken while it was still fluid to ensure homogeneity.

The first aim divides itself into a determination of: (1) the initial maximum value, (2) the minimum value and (3) the rate of recovery after shearing.

These determinations were made as follows: The maximum reading was obtained and the instrument was allowed to run until a minimum value was reached. It was considered that a reading which remained within 2 scale divisions (MacMichael degrees) for a period of 5 minutes was the minimum value for that rate of shear.

Consistency of Cream A

Sample	Initial Maximum reading*	Maximum obtained following an interval of rest after shearing to an arbitrary minimum of 135			Minimum reading
		1 min.	5 min.	35 min.	
I	210	167	175	189	126-128
II	230	166.5	179	188	125-127

*The readings given are in MacMichael degrees.

Evaluation of the results

1. The initial maximum readings were not in good agreement.
2. The minimum values were in good agreement.
3. The readings after a rest of 1 minute and over were in good agreement.

Inferences

1. Separate samples will have to be used for a repetition of the maximum readings, since the length of time for the recovery of the consistency of the sample is so long as not to be practicable.
2. It was considered that the difficulty in not obtaining reproducible maximum readings was due to the disturbance of the cream on packing into the viscometer cup.

To obtain a better maximum reading, two approaches were considered:

1. After placing the cream in the cup, it would be left for a period of one hour.

2. The cream could be packed so that it could be transferred as from a mold, thus causing a minimum of disturbance.

For the same batch of cream, the increase in temperature and the corresponding fall in consistency would be comparable after a given time after shearing.

The cream was allowed to rest after the minimum value had been obtained for a period of 1, 5, 15 and 30 minutes or until the maximum value was regained.

The results of the observations show that the recovery of the consistency was exceedingly slow, and it was decided not to wait for the final minimum value to examine the recovery of consistency. When an arbitrarily chosen minimum was reached, the instrument was turned off, and the bob moved manually back to zero deflection. The stop watch was then started for the interval of rest, after which the maximum value was re-determined. This method was discarded when later work showed that the rate of recovery could be more satisfactorily determined by the procedure outlined by Pryce-Jones. (see p. 11)

The first method was used on two new batches of cream, B and C.

The change of consistency of Creams B and C with time of shearing
(readings expressed in MacMichael degrees)

Time from the attainment of the maximum reading	Cream B			Cream C	
	I	II	III	I	II
0 sec.	257	248	248	230	226
15 "	194	195	192	168	164
30 "	183	184	181	159	153
45 "	176	178	175	153	147
60 "	171	173	169	148	143
90 "	164	165	163	142	135
120 "	159	161	160	137	131
150 "	155	158	156	133	127
180 "	152	155	154	132	125
210 "	150	153	153	130	---
240 "	148	150	150	128	---
270 "	146	150	150	127	---
300 "	145	150	150	126	---
Minimum reading	117	118	120	102	---

The recovery of consistency of Cream B

Sample	Initial Maximum reading	Maximum obtained following an interval of rest after shearing to an arbitrary minimum of 145					Minimum reading
		1 min.	5 min.	10 min.	20 min.	120 min.	
I	257	161	164	167	167	173	117
II	248	162	166	168	---	---	118
III	248	161	165	167	168	175	120

The recovery of consistency of Cream C

Sample	Initial Maximum reading	Maximum obtained following an interval of rest after shearing to an arbitrary minimum of 125				Minimum reading
		1 min.	5 min.	10 min.	20 min.	
I	230	137	142	143	144	102
II	226	137	140	143	146	---

Evaluation of the results

Though there was an appreciable difference between the results of creams B and C, the following general observations can be drawn:

1. The minimum values for each cream were in good agreement.
2. The maximum values were in fair agreement.
3. The rate of increase in consistency, though small, seemed in good agreement.

It is seen from creams A, B and C that the same batch of materials will produce creams of different characteristics even when prepared in a similar manner. It was considered that the degree of homogenization was probably the most likely cause of the differences.

To examine this possibility, the samples of cream B were mixed together —B(worked) and part was homogenized (B.2). Cream C was similarly treated.

A comparison of the consistency readings of worked and unworked samples of Creams B and C

Cream	Sample	Initial Maximum reading	Minimum reading
B.	I	257	117
	II	248	118
	III	248	120
B.(worked)	I	178	120
B.2	I	268	147
C.	I	230	102
	II	226	104
C.(worked)	I	185	101
C.2	I	242	---

It should be noticed that although the minimum value of both cream B and B (worked) and C and C (worked) are comparable, the rehomogenized cream B.2 gives a higher value. Creams D and E were prepared with the following results:

The change of the consistency of Creams B and C with time of shearing (readings are expressed in MacMichael degrees)

Time from the attainment of the maximum	Cream D					Cream E		
	I	II	III	IV	V	I	II	III
0 sec.	214	215	215	213	211	195	188	190
15 "	183	183	183	182	181	148	143	143
30 "	173	175	175	173	172	137	133	133
45 "	166	169	169	167	167	131	127	128
60 "	161	165	165	161	162	126	---	125

Inferences which can be drawn from creams A,B,C,D and E:

1. For each batch of cream, a maximum value within fair agreement can be obtained. It would seem, however, that some disturbance is caused in preparing the test sample. It would be preferable therefore if separate samples were kept which could be easily transferred.

2. The rate of fall of the readings are reproducible.

3. A minimum reading is repeatable on the same sample of cream from the same batch, on both the worked e.g. A.1 and B.1 and the unworked samples A and B, at the same rate of shear.

4. The degree of homogenization definitely affects the consistency reading.

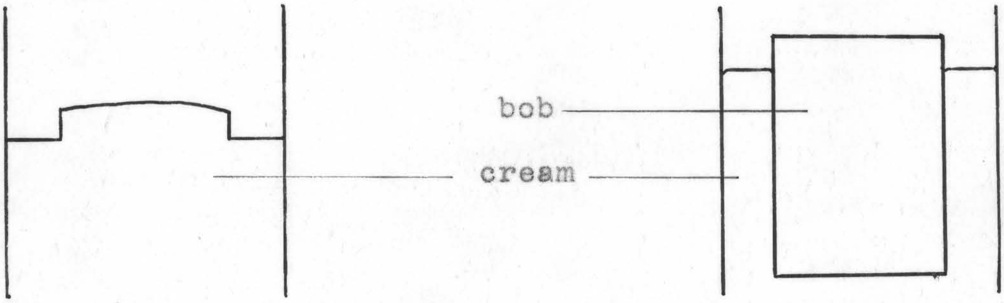
5. The rate of recovery of consistency seems fairly constant, though these have been determined possibly too close to the minimum value, with a result that the increase in the values for resting periods of 1 and 5 minutes are rather small.

6. The rate of recovery of consistency after is very slow.

The second method of attempting to obtain a more certain maximum value was tried, viz., the use of separate samples of approximately 150 G. which had been packed in the manner outlined below:

A crystallizing dish, the internal diameter of which closely approximates that of the cup of the viscometer, was lined with tin foil at the bottom and around the sides and filled with cream. It was shown that this could be turned upside down and the cream slid into the cup, the piece of tin foil now uppermost removed, and the foil around the sides smoothed out. The cream was thus introduced with a minimum of disturbance. The dishes were satisfactorily covered with a sheet of glass, the ground edge of the dish being smeared with a little grease. This produced an effective seal which prevented the cream from drying out. It had been shown previously, that by taking a flat ended spatula and rotating the cup around it, it was possible to produce a flat surface to the cream and leave an excess in the middle as in diagram (a) of Fig. 3. The introduction of the bob of the viscometer then produces a smooth upper surface and the cream adheres to a maximum extent to the outer part of the bob as in (b), whereas some of the earlier samples had presented an uneven appearance.

To test the method of packing the cream, the viscometer cup was filled when the dishes were packed, and the first reading therefore made on this sample.



(a) (b)

Diagram of the method used to indicate the preparation of the sample.

Figure 3

The change of the consistency of Cream F with time of shearing (readings are expressed in MacMichael degrees)

Time from the attainment of the maximum reading	Sample placed in the viscometer cup after preparation of cream	Sample transferred from dish into the viscometer cup	
	I	I	II
0 sec.	257	261	258
15 "	209	207	202
30 "	194	195	192
45 "	184	190	186
60 "	181	186	180
90 "	172	180	175
120 "	172	176	172
150 "	171	173	170
180 "	170	172	169
210 "	169	170	168
240 "	168	170	166
270 "	168	169	165
300 "	167	169	164
600 "	161	165	161
1200 "	156	156	153

The effect of the time of storage on the consistency of Cream F (readings are expressed in MacMichael degrees)

Length of storage Days	Initial Maximum reading	Minimum reading
1	257,261,258	158,162,161
3	248	156
4	248	155
6	253,247	157,152
11	240	149
13	238	148
14	242	149

Further evidence that the recovery of the initial maximum value is very slow, and that the minimum value is unaffected, is indicated in the following results from worked samples of cream F which had been repacked and left undisturbed for a number of days.

The effect of time of storage on the recovery of the consistency of worked samples of Cream F

Length of storage Days	Initial Maximum reading	Minimum reading
4	210	145
7	227	143
10	219	144
14	220	144
Original values of the unworked cream	240	148

The effect of the time of storage on the consistency of Cream G
(readings are expressed in MacMichael degrees)

Time from the attainment of the maximum reading	Time of storage of Cream G. in Days						
	1	2	4	4	5	7	22
0 sec.	222	229	207	210	209	216	211
15 "	181	191	170	173	165	180	165
30 "	171	179	163	163	153	169	158
45 "	166	173	158	159	149	163	153
60 "	162	170	154	156	149	160	149
75 "	159	167	153	152	147	156	146
90 "	157	164	150	150	146	153	144
105 "	155	162	149	149	144	151	141
120 "	154	160	148	147	143	150	140
150 "	151	157	146	145	141	147	137
180 "	149	156	144	142	138	145	134
210 "	149	154	143	140	137	144	134
240 "	149	154	143	139	135	142	133
270 "	148	152	142	138	135	141	133
300 "	147	152	142	137	133	138	133
360 "	147	150	140	137	131	139	133
420 "	146	149	140	136	129	138	133
480 "	144	148	139	135	128	137	133
540 "	145	147	138	134	127	136	132
600 "	145	147	137	133	133	136	131

The two batches of cream, F and G, would seem to indicate that there is a fall in reading for the first few days, until a steady value is obtained.

The conclusions which can be drawn from the batches of cream A,B,C,D,E,F and G show:

1. Results from the same batch of cream are replicable; i.e. a maximum value, a fall in consistency, a minimum value and a recovery of consistency can be obtained on new samples.
2. It is necessary to use separate samples for each determination, since the maximum value is not reproducible on a worked sample, although the minimum value can be repeated.
3. Different batches of cream give different results.

The effect of homogenization

A new batch of cream was prepared using a different batch of bentonite. A slight modification in the procedure was adopted, in an attempt to obviate any possibility of difference in the manufacture of the cream; the bentonite was weighed on an analytical balance and gelled separately. The cream was prepared as in the previous samples and passed through the hand homogenizer to give samples which had been homogenized, 4,6,8,10 and 16 times.

The effect of homogenization on the consistency of Cream M showing the change in consistency with time of shearing. (readings are expressed in MacMichael degrees)

Time from the attainment of the maximum reading	Times homogenized	4	6	8	10	16	16	16	16
	Storage in Days	(11)	(3)	(3)	(3)	(1)	(1)	(2)	(2)
0 sec.		209	243	277	313	346	343	331	330
15 "		165	202	222	243	282	276	262	265
30 "		154	187	210	237	268	274	252	262
45 "		150	183	207	230	272	272	257	265
60 "		148	182	206	228	268	270	270	265
75 "		146	181	205	223	262	266	267	270
90 "		144	180	203	221	260	262	263	265
105 "		143	178	202	220	255	258	260	265
120 "		143	177	200	228	255	255	257	265
150 "		141	175	200	228	260	253	257	---
180 "		140	174	197	221	262	248	257	257
210 "		139	172	197	224	260	252	257	262
240 "		138	172	196	224	257	257	257	257
270 "		137	172	195	222	255	260	257	252
300 "		136	172	195	223	257	257	255	252

The effect of homogenization on the consistency of Cream N showing the change in consistency with time of shearing. (readings are expressed in MacMichael degrees)

Time from the attainment of the maximum reading	Times homogenized	4	4	8	12	16	16	16	20
	Storage in Days	(2)	(2)	(2)	(3)	(3)	(4)	(9)	(8)
0 sec.		292	288	354	347	362	341	333	336
15 "		240	239	296	282	295	267	286	270
30 "		218	216	271	257	280	253	275	257
45 "		210	210	265	251	267	253	270	259
60 "		209	211	260	246	257	253	267	254
75 "		208	206	254	---	253	265	265	253
90 "		205	205	253	248	253	267	261	250
105 "		204	203	252	---	---	267	259	253
120 "		204	203	252	244	---	258	257	260
150 "		200	201	247	---	258	265	251	262
180 "		197	200	245	240	268	265	257	263
210 "		195	199	244	---	---	262	257	262
240 "		194	199	243	242	254	260	253	258
270 "		194	198	243	---	---	258	250	260
300 "		195	---	240	242	250	260	250	258

The reproducibility of the results is well shown with the results obtained from cream M which had been homogenized 4 times.

The change of the consistency with the time of shearing
of Cream M homogenized 4 times
(readings are expressed in MacMichael degrees)

Time from the attainment of the maximum	Readings made 8 days after preparation						
	I	II	III	IV	V	VI	Average
0 sec.	210	209	206	209	212	209	209
15 "	163	162	162	165	166	166	164
30 "	155	152	152	155	154	157	154
45 "	150	149	148	152	150	153	150
60 "	147	146	144	150	148	150	147
75 "	145	144	142	149	147	147	145
90 "	143	142	140	146	145	145	143
105 "	141	141	137	144	144	143	142
120 "	140	140	138	143	142	143	141
150 "	138	139	138	140	140	141	139
180 "	137	137	136	139	138	141	138
210 "	135	136	136	137	137	138	136
240 "	135	135	134	137	137	137	135
270 "	134	134	133	136	136	136	135
300 "	133	134	132	136	135	135	134

The results therefore indicate that, for the hand homogenizer, it is necessary to homogenize the cream some 16 times before the limit of the consistency is reached. Naturally this is a laborious and very inconvenient method, so that other types of apparatus were considered, viz., the colloid mill and the Waring blendor. Both of these machines tend to incorporate a large quantity of air, which is most unsatisfactory. The Waring blendor, in addition, can only homogenize about 400 G. at one time. It was decided, therefore, to motorize the hand homogenizer and this relieved the tedium of repeated homogenization.

Cream Q was prepared in the usual manner, but was divided into two portions for homogenization:

1. The hand homogenizer was used and the cream examined in the usual manner to confirm the previous results.

2. The colloid mill was used and the product was later de-aerated in a vacuum desiccator until free from air. A number of samples of this cream were then autoclaved, the jars being weighed before and after the autoclaving, so that any loss which occurred could be detected and the sample discarded.

The autoclaved and the unatoclaved creams were then examined in the following ways:

1. The usual procedure was used.

2. The method advocated by Pryce-Jones, which was referred to earlier, to distinguish between anomalous behavior was also used to indicate the recovery after shearing.

3. The Interchemical rotational viscometer was used.

The change of consistency with time of shearing of Cream Q
homogenized 16 times
(readings are expressed in MacMichael degrees)

Storage in Days	(1)	(1)	(3)	(3)
Time from the attainment of the maximum reading	I	II	I	II
0 sec.	351	347	333	330
15 "	290	282	265	257
30 "	279	275	252	248
45 "	273	273	252	248
60 "	270	273	258	248
75 "	264	268	262	---
90 "	264	270	260	252
105 "	264	260	265	---
120 "	260	257	267	250
150 "	257	260	265	250
180 "	260	260	262	248
210 "	265	265	262	252
240 "	265	270	262	255
270 "	265	270	260	257
300 "	265	270	258	257

The change of consistency reading with time of shearing
of Cream Q prepared in the colloid mill
(readings are expressed in MacMichael degrees)

Time from the attainment of the maximum reading	
0 sec.	133
5 "	121
10 "	119
15 "	118
20 "	115
25 "	114
30 "	113
35 "	113
40 "	112
45 "	111
50 "	111
55 "	111
60 "	110

The effect of autoclaving

Cream Q (colloid mill, autoclaved)

The creams were autoclaved at 120°C., for a given period of time, and packed in the usual manner when cold. The samples which were autoclaved at different times are indicated as: I, II, III, IV, and V.

The change in consistency with time of shearing, of autoclaved samples of Cream Q prepared in the colloid mill

Time autoclaved	30 minutes			2 hours	
Storage in Days	(1)	(2)	(2)	(3)	(4)
Sample	I	II	III	IV	V
Time from the attainment of the maximum reading					
0 sec.	342	346	360	358	362
5 "	258	---	265	268	---
10 "	245	240	252	254	262
15 "	238	233	243	245	253
20 "	---	226	239	242	245
25 "	---	220	233	236	241
30 "	225	217	234	233	236
35 "	---	211	232	230	236
40 "	---	210	231	226	233
45 "	221	207	229	223	231
50 "	---	205	227	219	229
55 "	---	204	226	218	227
60 "	214	203	223	214	223
75 "	212	198	216	209	218
90 "	210	194	214	204	217
105 "	207	190	---	202	215
120 "	204	188	212	200	213
150 "	199	---	208	---	---
180 "	195	174	210	195	203
210 "	190	---	---	---	---
240 "	187	168	204	191	199
270 "	183	---	---	---	---
300 "	179	162	195	188	194
Minimum reading	170		170	170	165

The recovery of the consistency in the autoclaved and unautoclaved cream Q prepared in the colloid mill is shown in the following table.

Cream Q (colloid mill)

The bob of the viscometer was held at a deflection of 110 MacMichael degrees for a period of rest after shearing, when the change in reading with time was recorded.

The increase in consistency following a period of rest after shearing in Cream Q prepared in the colloid mill
(Method after Pryce-Jones)

Time from the original deflection	Change of the deflection with time after a period of rest following shearing		
	0 min.	15 min.	90 min.
0 sec.	110	110	110
5 "	68	81	102
10 "	65	74	97
15 "	63	70	93
20 "	62	68	90
25 "	61	67	88
30 "	61	66	86
35 "	--	65	85
40 "	--	65	83
45 "	--	64	82
50 "	--	64	81
55 "	--	64	81
60 "	59	63	80
120 "	--	62	76
300 "	--	60	72
600 "	--	59	70

The increase in consistency following a period of rest after shearing in Cream Q prepared in the colloid mill and autoclaved (Method after Pryce-Jones)

Time from the original deflection	Change of the deflection with time after a period of rest following shearing		
	0 min.	5 min.	60 min.
0 sec.	160	160	160
5 "	102	116	126
10 "	89	100	106
15 "	81	89	95
20 "	75	82	86
25 "	70	76	80
30 "	67	72	75
35 "	64	69	71
40 "	61	66	68
45 "	59	64	66
50 "	58	62	63
55 "	56	60	62
60 "	55	59	60
90 "	50	--	54
120 "	48	--	51

The autoclaving of cream Q on three different occasions for 30 minutes and on a further sample for 2 hours, produces creams which give very similar maximum values. It should be noted that there is a marked increase in reading, over the unautoclaved cream, and it may be significant that the maximum value obtained is comparable with the values obtained by homogenization of the cream to a constant value. The minimum values obtained are, however, appreciably lower than those of the cream homogenized 16 times.

The increase in the consistency of the emulsion, which occurred on autoclaving, is quite marked and can hardly be expected. A parallel may be found, however, in the behavior of milk and cream, and possibly also of rubber.

The introduction of pasteurization into commercial dairy practice has since its inception been known to decrease the consistency of raw cream. A method to increase the consistency of pasteurized cream, known as rebodying, was introduced by Dahlberg following its observation by Kloser. The process consists essentially in a cooling of the cream after pasteurization followed by a re-warming to 86°F. and a further cooling.

There have been three main mechanisms suggested to explain the behavior:

1. A hydration of the colloidal matter occurs.
2. A lattice structure is formed by the globulin which enmeshes fat globules and so produces clustering.
3. An adsorption of certain substances e.g. phospholipides occurs on the fat globules.

A similar clustering is stated to take place in rubber latex and it is considered that a lattice structure is produced from the colloidal matter in the dispersion medium which enmeshes globules and thus produces an increased consistency. It is conceivable therefore to imagine a clustering of the oil globules, in this bentonite containing emulsion, produced by retention of the globules in a fibrillar network.

Three possible explanations can be considered to account for the increase in consistency:

1. An increase in the effective amount of the dispersed phase in respect to the dispersion medium may have been produced, as for example, by the presence of an adsorbed film on the oil globules.

Recent work by Robinson has confirmed that the viscosity of a suspension of glass spheres in various media can be attributed to an increase in effective size of the spheres by adsorption of a halo of dispersion medium, with a resultant diminution of the effective amount of dispersion medium. (31)

2. An increase in structural viscosity may have been produced by a flocculation of the oil globules. Many workers have shown that flocculation of particles produces an increase in viscosity, or in other words the complete dispersion of particles produces a lowered viscosity. (26)(30)(32)(33)

3. An increase in the amount of the dispersed phase may have occurred through the formation of a dual emulsion.

Creams prepared without bentonite

In an attempt to study the role of bentonite in the stabilization of the emulsion to temperatures necessary for sterilization, viz., 120°C. for 30 minutes, two batches of cream were prepared without bentonite. The cream was prepared in the same manner as for the previous batches containing bentonite.

Formula:

Cetyl alcohol	5.0
Liquid petrolatum	25.0
Sodium lauryl sulfate	0.5
Bentonite	---
Distilled water	to 100.0

The method of testing was that as previously outlined:

1. The change of reading with time at a given r.p.m.

2. The change of reading with time after definite intervals of rest, after the cream has been sheared to its minimum value.

3. The method advanced by Green was used with the Interchemical rotational viscometer.

The effect of homogenization of Creams V and W prepared without bentonite.
(readings are expressed in MacMichael degrees)

Time from the attainment of the maximum reading	Cream V		Cream W	
	Times homogenized		Times homogenized	
	1	4	1	4
0 sec.	177	183	158	182
5 "	134	154	120	156
10 "	132	150	117	151
15 "	129	146	113	148
20 "	126	144	111	146
25 "	123	142	108	144
30 "	121	140	106	143
35 "	118	139	103	142
40 "	117	138	102	141
45 "	116	137	101	140
50 "	115	136	99	139
55 "	114	136	98	138
60 "	114	135	97	137
90 "	109	132	--	134
120 "	106	129	90	132
180 "	102	126	88	131
240 "	101	124	86	129
300 "	100	123	85	127
Minimum reading	---	120	--	122

The increase in consistency of Cream V and W following a period of rest after shearing (Method after Pryce-Jones)

Time from the original deflection	Change of the deflection with time after a period of rest following shearing							
	Cream V				Cream W			
	Times homogenized				Times homogenized			
	1		4		1		4	
	0 min.	30 min.	0 min.	30 min.	0 min.	90 min.	0 min.	30 min.
0 sec.	100	100	100	100	100	100	100	100
5 "	42	44	58	60	41	43	56	62
10 "	34	35	50	48	33	34	46	52
15 "	30	31	43	42	30	30	40	45
20 "	28	28	39	38	27	27	37	41
25 "	26	26	36	35	26	26	34	38
30 "	25	25	33	33	25	25	33	36
35 "	24	24	32	32	24	24	31	34
40 "	24	23	31	30	23	23	30	33
45 "	23	23	30	29	22	22	29	31
50 "	23	22	29	28	22	22	28	31
55 "	22	22	28	27	21	21	27	30
60 "	22	21	27	27	21	21	27	29
90 "	20	20	24	23	20	19	24	26
120 "	19	19	21	21	19	18	23	25
180 "	18	18	20	20	17	17	22	24
240 "	18	17	20	20	16	16	21	23
300 "	17	17	19	19	16	16	21	22

The change in the consistency reading was noted in a sample of cream V.4 which had not been sheared previously. The values are recorded in the following table.

A comparison of sheared and unsheared Cream V. homogenized 4 times

Time from original deflection	Deflection of the unsheared cream	Deflection of the sheared cream after 30 min. period of rest after shearing
0 sec.	100	100
5 "	72	60
10 "	60	48
15 "	50	43
20 "	44	38
25 "	39	36
30 "	36	34
35 "	33	32
40 "	31	30
45 "	29	29
50 "	28	28
55 "	28	28
60 "	27	27

The effect of homogenization

The creams V.4 and W.4 were mixed together and homogenized to give a cream which had been homogenized eight times - VW.8. The usual readings were made and are recorded in the table below with comparable values of creams homogenized once and four times.

A comparison of Cream V and W homogenized 1, 4 and 8 times

Cream	No. of times homogenized	Maximum reading	Reading after 5 min.	Minimum reading
V	1	177	100	---
W	1	158	85	---
V	4	182	122	112
W	4	175	118	113
V	4	183	123	120
W	4	182	127	122
VW	8	180	112	110
VW	8	177	120	115

The early work on a cream without bentonite had been carried out on the following formula:

Formula:

Cream U		Bentonite cream
Cetyl alcohol	7.0	5.0
Liquid petrolatum	35.0	25.0
Sodium lauryl sulfate	0.7	0.5
Bentonite	---	2.0
Distilled water	to 100.0	100.0

The ratio of the liquid petrolatum: cetyl alcohol: sodium lauryl sulfate, had been maintained the same, but to allow for the reduced consistency their percentages had been increased. Cream U on homogenization, however, gave a larger deflection than had been expected and in order to prevent permanent damage to the viscometer wire, a sample of 90 G. was used in the tests with the MacMichael viscometer. The usual readings were taken and are recorded below.

The change of consistency with time of shearing of Cream U.*
(readings are expressed in MacMichael degrees)

Time from the attainment of the maximum reading	
0 sec.	327
15 "	302
30 "	264
45 "	252
60 "	246
75 "	240
90 "	236
105 "	238
120 "	232
150 "	228
180 "	223
240 "	220
300 "	220

*90G. of cream was used for this test.

The increase in consistency following a period of rest after shearing of Cream U. (Method after Pryce-Jones)

Time from the original deflection	Change of the deflection with time after a period of rest following shearing				Previously unsheared cream
	0 min.	15 min.	0 min.	90 min	
0 sec	200	200	200	200	200
5 "	108	110	108	114	142
10 "	82	84	82	88	112
15 "	72	74	70	75	93
20 "	66	67	64	68	80
25 "	62	63	60	65	72
30 "	59	60	57	62	66
35 "	57	57	54	58	62
40 "	55	55	53	56	59
45 "	53	53	51	54	56
50 "	52	51 -	49	53	54
55 "	51	50	48	51	52
60 "	50	49	47	50	51
90 "	46	45	--	--	45
120 "	44	42	--	--	44

The results on cream U are included, because the cream has been tested on the Interchemical rotational viscometer.

The following comparison of two creams, with and without bentonite, was made on the MacMichael and the Interchemical Rotational viscometers.

Formulae:	Cream X.16	Cream Y.4
Cetyl alcohol	5.0	5.0
Liquid petrolatum	25.0	25.0
Sodium lauryl sulfate	0.5	0.5
Bentonite	2.0	---
Distilled water	to 100.0	100.0

Cream X.16

MacMichael Viscometer

The change of consistency with time of shearing of Cream X

Time from the attainment of the maximum.	Cream homogenized 16 times
0 sec.	348
5 "	308
10 "	292
15 "	287
20 "	282
25 "	277
30 "	273
35 "	271
40 "	268
45 "	267
50 "	265
55 "	260
60 "	250
90 "	251
120 "	247
180 "	240
240 "	236
300 "	234
Minimum reading	225

Interchemical Viscometer

U_{100} = 8.15 poise

U_{200} = 4.99 poise

f_{100} = 1280 dynes/sq.cm.

f_{200} = 1300 dynes/sq.cm.

Cream Y.4

MacMichael Viscometer

The change of consistency with time of shearing of Cream Y

Time from the attainment of the maximum	Cream homogenized 4 times
0 sec.	189
5 "	157
10 "	149
15 "	147
20 "	144
25 "	142
30 "	141
35 "	140
40 "	138
45 "	137
50 "	136
55 "	135
60 "	134
90 "	128
120 "	124
180 "	121
240 "	118
300 "	115
Minimum reading	111

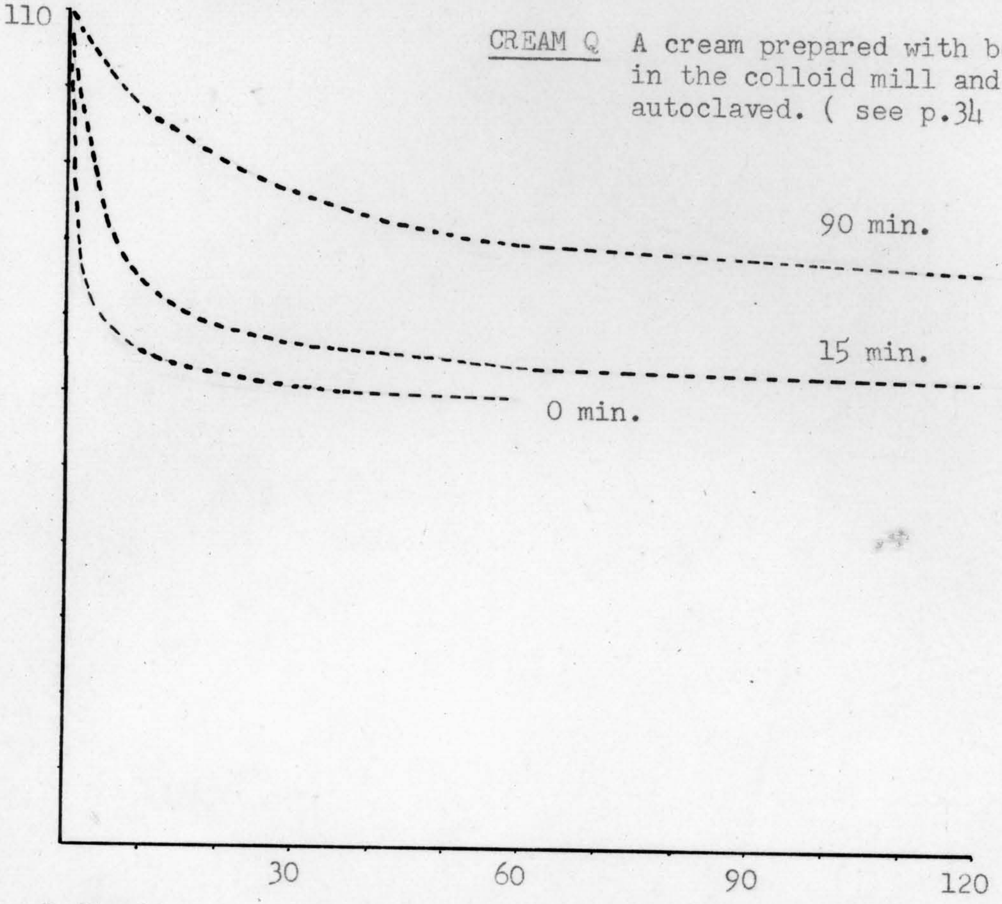
Interchemical Viscometer

The method used by Green indicates a pseudoplastic nature, and if the limiting viscosity at high shear is taken, the value would be around 3 poise.

The data from the Interchemical rotational viscometer is insufficient to draw any definite conclusions, though the following indications would appear justifiable:

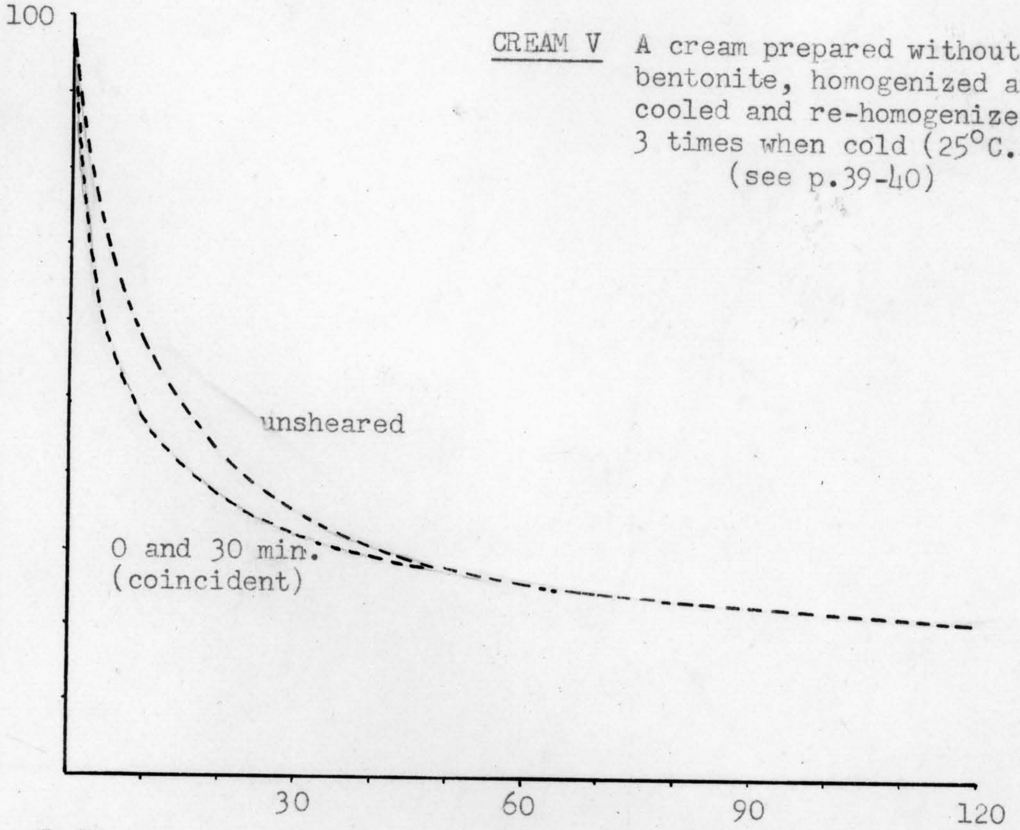
1. The cream without bentonite exhibits pseudoplasticity, and shows appreciable thixotropic breakdown. The full curve would be necessary to characterize the substance.

2. The cream containing bentonite exhibits plasticity and can be characterized by the coefficient of 'plastic viscosity' U determined at two rates of shear, and by the yield value f also determined at two rates of shear.



CREAM Q A cream prepared with bentonite in the colloid mill and autoclaved. (see p.34)

Deflection in MacMichael degrees against time in seconds.

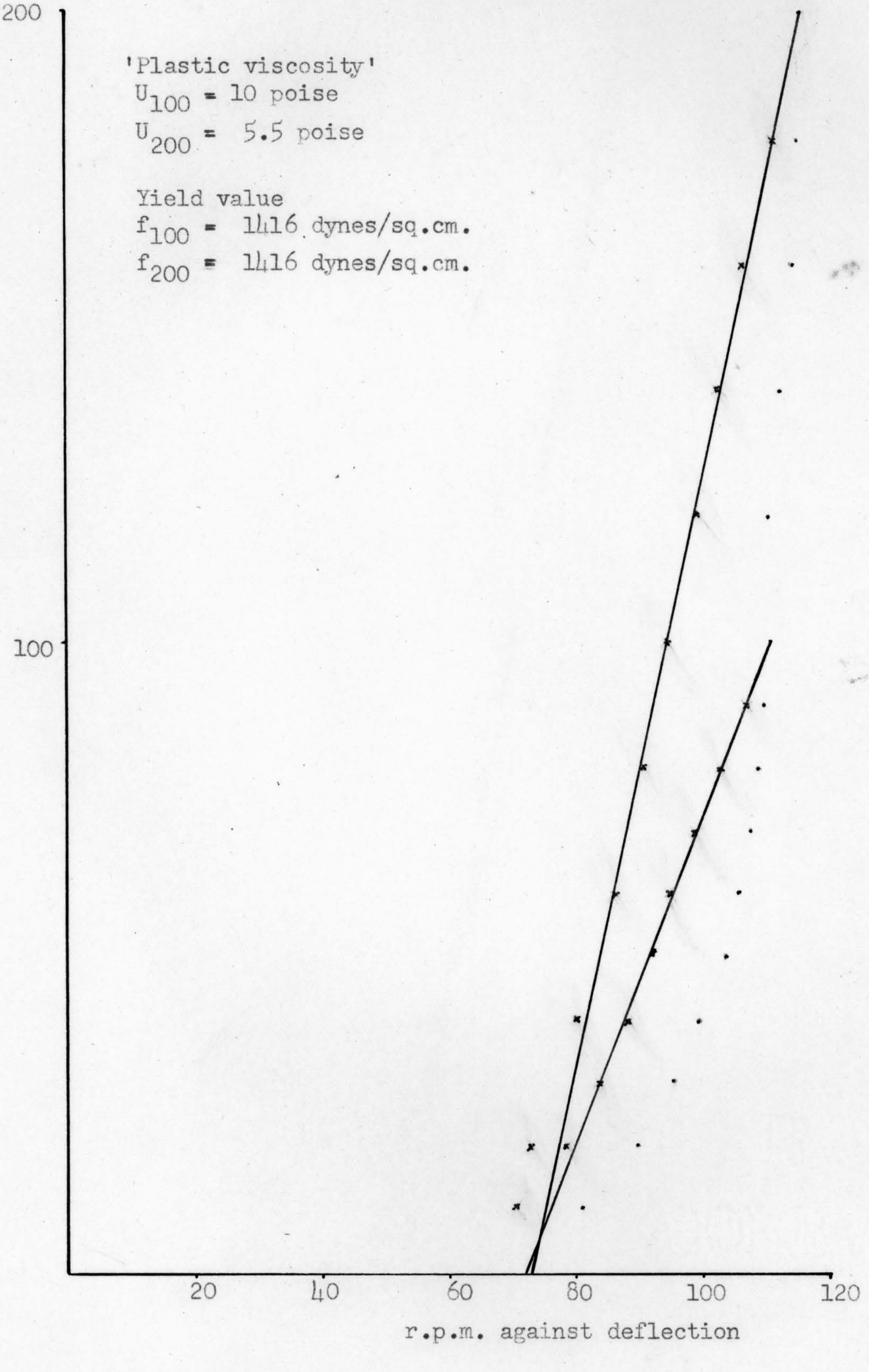


CREAM V A cream prepared without bentonite, homogenized and cooled and re-homogenized 3 times when cold (25°C.). (see p.39-40)

Deflection in MacMichael degrees against time in seconds.

CREAM Q — Interchemical Rotational Viscometer

A cream prepared with bentonite in the colloid mill and autoclaved.



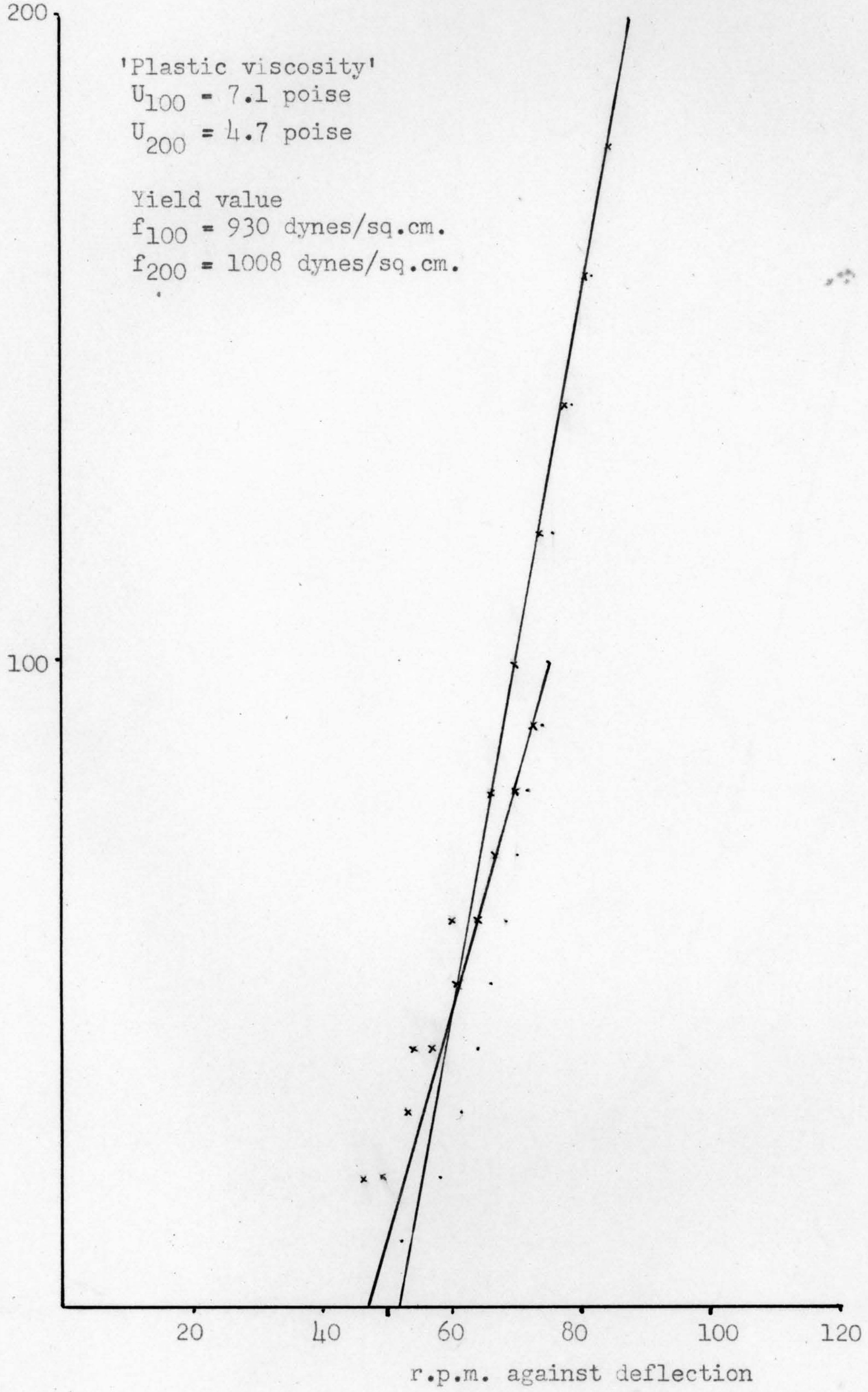
'Plastic viscosity'
U_{100} = 10 poise
U_{200} = 5.5 poise

Yield value
f_{100} = 1416 dynes/sq.cm.
f_{200} = 1416 dynes/sq.cm.

r.p.m. against deflection

CREAM Q Interchemical Rotational Viscometer

A cream prepared with bentonite in the colloid mill.



'Plastic viscosity'

U_{100} = 7.1 poise

U_{200} = 4.7 poise

Yield value

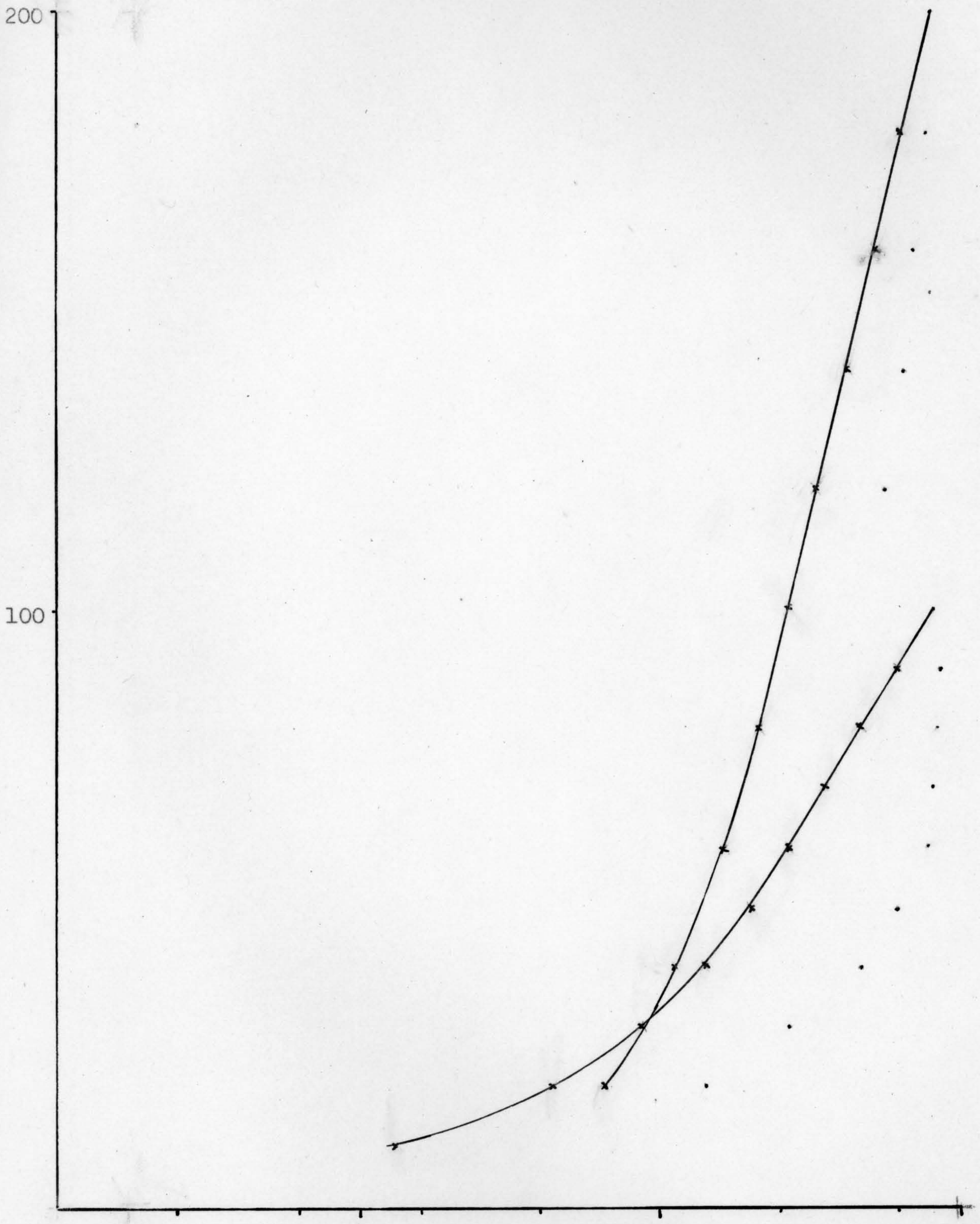
f_{100} = 930 dynes/sq.cm.

f_{200} = 1008 dynes/sq.cm.

CREAM U

Interchemical Rotational Viscometer

A cream prepared without bentonite, homogenized and cooled.

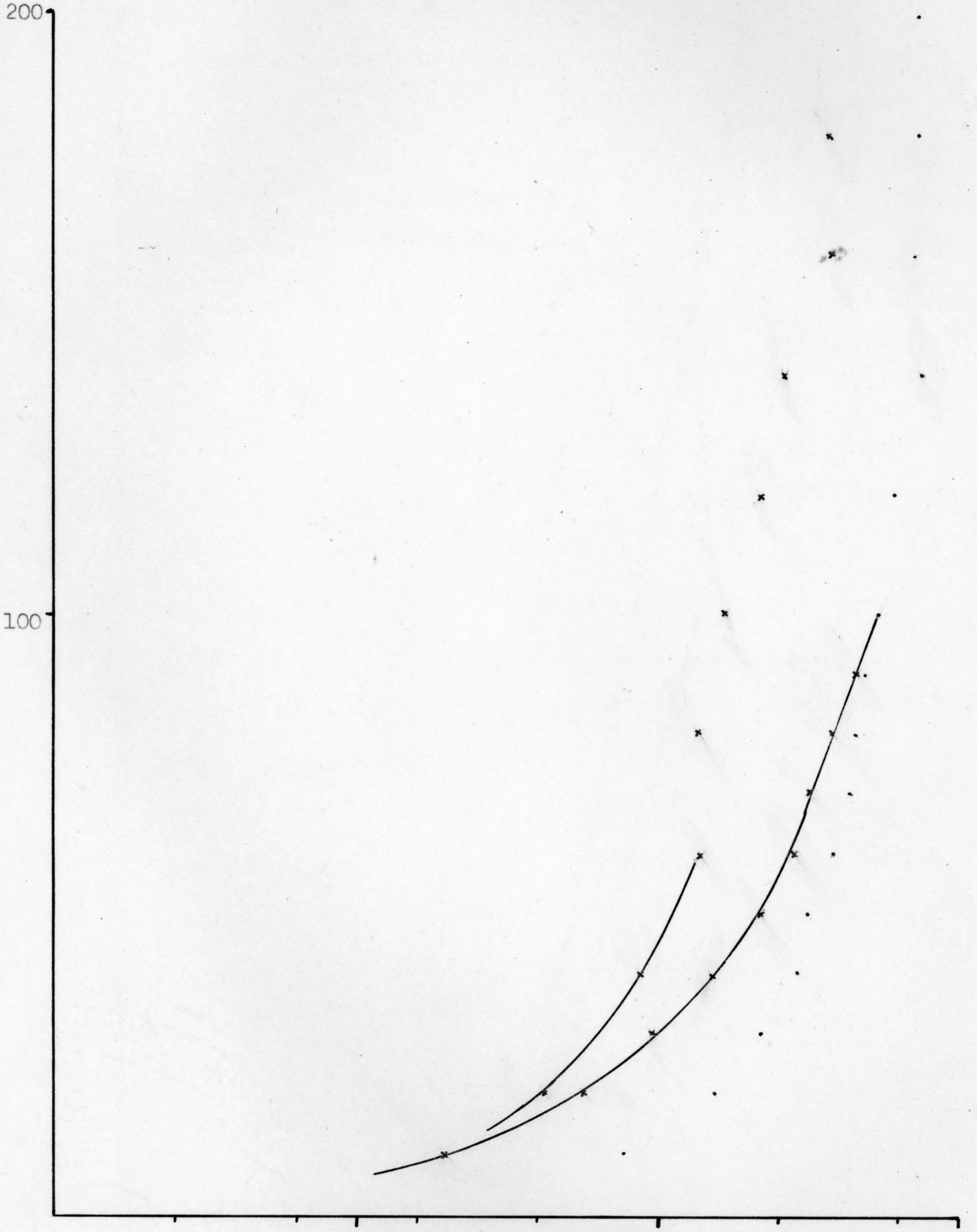


r.p.m. against deflection

CREAM U

Interchemical Rotational Viscometer

A cream prepared without bentonite, homogenized and cooled and re-homogenized 3 times when cold (25°C.).

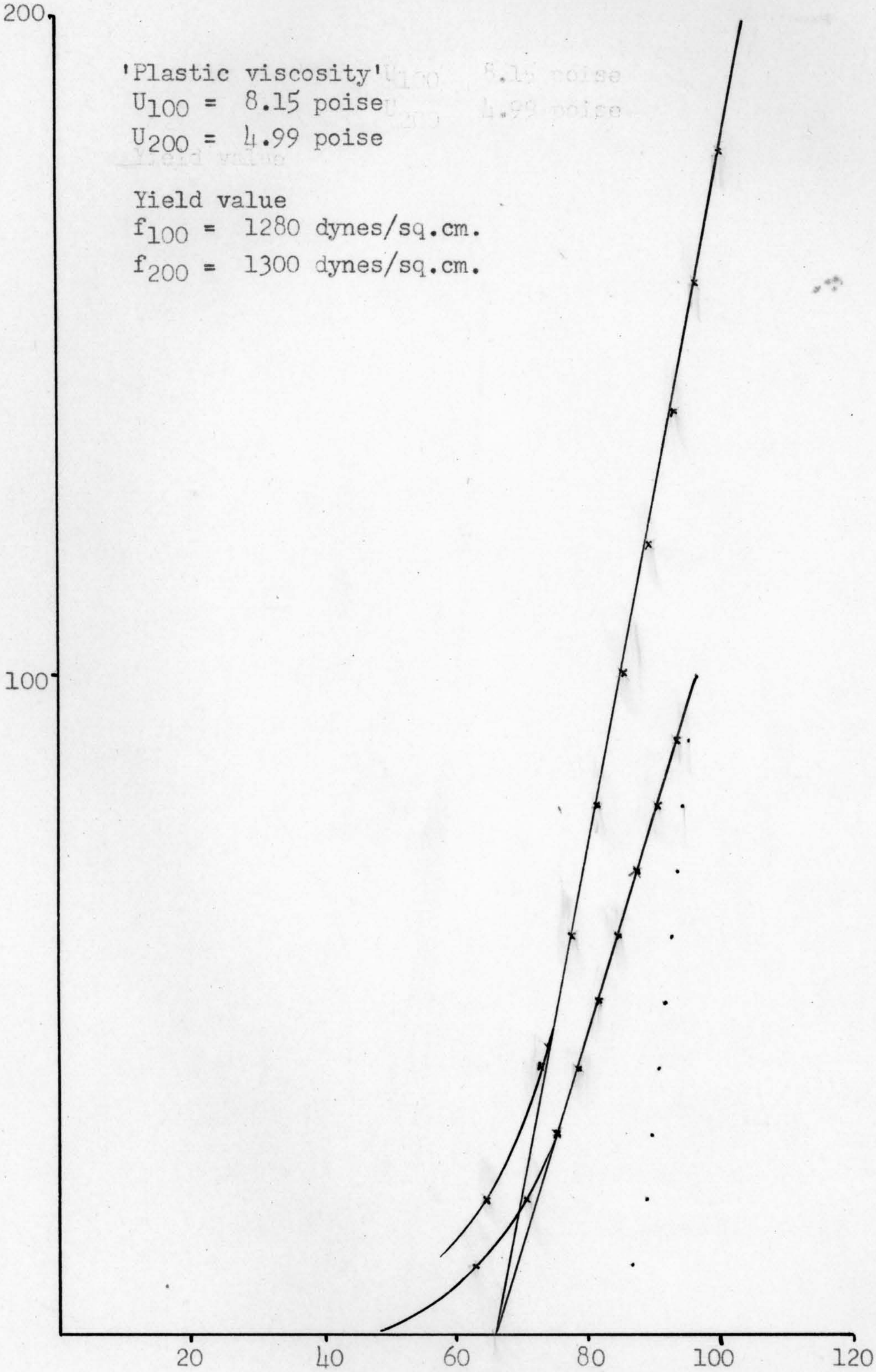


r.p.m. against deflection

CREAM X

Interchemical Rotational Viscometer

A cream prepared with bentonite, homogenized and cooled and re-homogenized 15 times when cold (25°C.).



'Plastic viscosity'

U_{100} = 8.15 poise

U_{200} = 4.99 poise

Yield value

f_{100} = 1280 dynes/sq.cm.

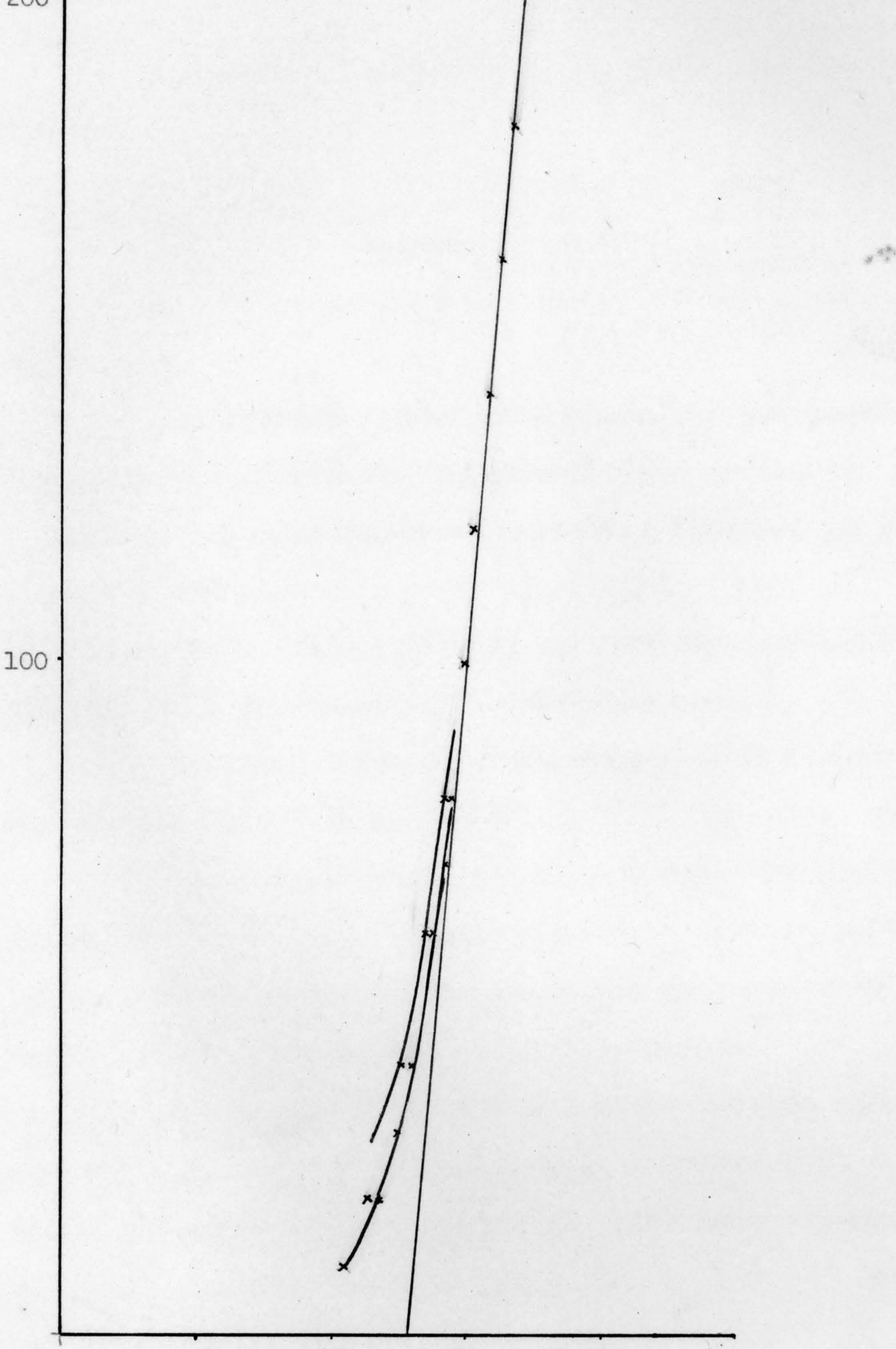
f_{200} = 1300 dynes/sq.cm.

r.p.m. against deflection

CREAM Y

Interchemical Rotational Viscometer

A cream prepared without bentonite, homogenized and cooled and re-homogenized 3 times when cold (25°C.).



r.p.m. against deflection

GENERAL CONCLUSIONS

A comparison of two creams prepared according to the formulae:

Cetyl alcohol		5.0	5.0
Liquid petrolatum		25.0	25.0
Sodium lauryl sulfate		0.5	0.5
Bentonite		2.0	---
Distilled water	to	100.0	100.0

can be made.

1. The consistency of both creams is increased on homogenization, and, for the homogenizer available, reaches a limiting value which is more readily attained in the cream without bentonite.

2. A much higher initial maximum consistency is attained with the bentonite-containing cream.

3. The consistency of both creams can be reproduced if the same materials are available.

4. After the creams have been sheared to their limiting value, the build up of consistency with time is quite marked in the bentonite-containing cream and only observed to a very small extent in the cream without bentonite.

5. The bentonite-containing cream remains stable to autoclaving, and may actually show an increase in consistency, while the cream without bentonite shows some separation of oil, and a granular appearance after the oil has been redispersed by shaking.

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DATE:

January 22, 1952