

1937

# Studies on the physical-chemical properties of honey

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STUDIES ON THE PHYSICAL-CHEMICAL  
PROPERTIES OF HONEY

By

John Covington Williams

A Thesis Submitted to the Graduate Faculty  
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject - Bio-Physical Chemistry

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1937

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## I. INTRODUCTION

The physical and chemical properties of honey may be divided, for the purpose of study, into two parts, those belonging to a concentrated aqueous solution of levulose and dextrose, and those arising from the presence of colloidal material. Inasmuch as the properties of sugar solutions are well known and open to wider investigation, the following study is more directly concerned with the colloidal systems present in honey.

One of the more striking properties of honey is its high viscosity. The magnitude of the viscosity is largely dependent on the water content, but its character is the result of the colloidal system present. There are two phenomena connected with viscosity of honey that are of special significance in this respect. First, a honey may behave in an anomalous fashion, showing an apparent viscosity which is a function, between limits, of the rate of shear or shearing stress involved in the measurement. Second, the apparent viscosity of a honey may be much less immediately after stirring, the viscosity increasing to a constant value on standing. This general phenomenon has been termed thixotropy by Freundlich (1928).

The research presented in this thesis deals with quantitative studies on several American honeys, with special reference to the phenomena of variable viscosity and thixotropy. The honeys have been rated on this basis and these ratings



correlated with their composition.

Information concerning the thixotropy and anomalous viscosity of an honey is expected to be valuable in predicting its foaming characteristics, since excessive foaming has been shown by Paine and Lothrop (1935) to be directly related to the amount of colloidal material present. It should also be helpful in predicting granulation behaviour as far as this is conditioned by the presence of protective substances. The apparatus involved in the determination of anomalous viscosity and thixotropy is relatively available to the honey producer and furthermore is fundamental to viscosity control, a feature of honey production that has been unwarrantably neglected.

## II. HISTORICAL

### A. Review of Thixotropy

Before discussing the general properties in honey, a review of thixotropy and anomalous viscosity is in order. The term thixotropy, originated by Freundlich, is derived from the Greek 'to touch' and 'to change', and refers to the reversible sol-gel transformation brought about by stirring. An excellent review of the subject has been made by Pryce-Jones (1934).

Perhaps the earliest recorded observation of thixotropy was that by Kuhne in 1863 who described a nematode which wandered through a muscle cell and traversed the cross-striated fibers without apparent effort. The movement seemed to liquify the striations, but they set anew after the nematode had passed.

Thixotropy is shown by ferric oxide sol, which was studied by Szegvari and Schalek (1923). If a small amount of an electrolyte is added to a concentrated ferric oxide sol it rapidly sets to a gel of high rigidity. This gel is easily convertible to a sol by shaking and sets again in a few seconds. The process can be continued almost indefinitely. Ultramicroscopic observations show the particles of the colloid to be separate in the gel form, but not showing Brownian motion as they do in the sol form.

Aluminum oxide sol shows properties similar to those of

the ferric oxide sol. In this case, the thixotropy is accompanied by double refraction. Addition of excess electrolyte causes disappearance of this optical property as well as the thixotropy. Hauser (1929) observed a dialysed bentonite solution, which has no thixotropic properties, at such a low concentration that each individual particle was visible under the ultramicroscope. The particles were in active Brownian motion, but on addition of a trace of electrolyte the movement ceased instantly, though the particles were separated by a distance of 20  $\mu$ . Particles of another sol added to such a suspension did not approach the bentonite particles but rebounded at considerable distance. These, as well as other observations have led Hauser (1931) to the hypothesis that thixotropy is induced by the presence of solvated 'hulls' around each particle.

Pryce-Jones (1934) states, "We shall obtain a more accurate conception of the nature of thixotropy if we cease to regard a compound as 'Thixotropic' or 'Non-Thixotropic', but adopt the idea that the 'Thixotropic state' can be assumed by a very large number of compounds under appropriately chosen conditions. Thixotropy is a phenomenon that should be associated with the colloidal environment rather than the intrinsic properties of the dispersed particles; it represents one of the manifold of states which a colloidal system can assume in passing from a state of complete peptisation to a state of complete

precipitation. It is a well established fact that thixotropy is more pronounced in systems containing non-spherical particles. . . . . It must be emphasized that thixotropy refers to a reversible process."

According to Freundlich and Rawitzer (1927), one of the most characteristic features of thixotropic systems is the relationship which exists between their setting time and the cross section of the vessel in which they are contained. The time of setting of a thixotropic gel in a cylindrical vessel increases with increasing diameter: thus a particular bentonite gel set in a few seconds in a test tube of one centimeter diameter, but the same gel required over an hour to set in a beaker of five centimeters diameter. The solid content of a bentonite gel necessary to give the same setting time increases as a linear function of the diameter of the container. Pryce-Jones (1934) confirmed the influence of the diameter of the vessel on the setting time of a thixotropic enamel.

In the discussion following the paper of Pryce-Jones (1934), he mentions that a sample of honey from the moors of Durham, England, was well stirred and poured into a cylindrical jar 4.5 centimeters in diameter to a depth of 3.5 centimeters. The jar was left to stand for a week and then inverted. No apparent flow could be observed after six weeks. A control experiment showed that the honey flowed readily after two or three rapid shakes, at the end of six weeks.

In a true fluid the viscosity is independent, by definition, of the rate of shear. In many actual systems, however, the apparent viscosity is a function of the rate of shear. Bingham (1922) p. 317 has studied 'plastic' substances which show a yield value; that is, a definite force must be exceeded before flow commences. He finds that the same results are obtained whether observations are made proceeding from low to high rates of shear or vice versa. In a thixotropic system, however, its properties cannot be represented by a single curve connecting apparent viscosity and rate of shear. By definition, the apparent viscosity of a thixotropic system is immediately changed by any flow however small and an appreciable time is necessary for its restoration to its former value. Furthermore, the apparent viscosity is a function of the time it has been left at rest after shearing has ceased.

According to Pryce-Jones (1936a), in comparing the apparent viscosity of a thixotropic gel at various intervals of time after shearing has ceased, it is essential to measure the viscosity at the same rate of shear. If the measurements are made at different rates of shear the results have no quantitative value as the relationship between viscosity and rate of shear has not been established. "This condition," states Pryce-Jones, "precludes the use of the falling sphere viscometer, the capillary tube or the Searle type of viscometer for comparisons of the viscosities of thixotropic systems at different setting

times. It will therefore be evident that the quantitative comparison of the viscosities of thixotropic systems involves considerable theoretical difficulties. As far as the author is aware, no quantitative data based on sound theoretical assumptions have yet been published."

DeBoer and Kniphorst (1932) found that stirred heather honey from Calluna vulgaris and to a lesser extent from Erica cinerea showed an increase in viscosity on standing as shown by time of extrusion per gram from a Holde viscometer. Ordinary honeys did not exhibit this behaviour. Scott Blair (1935) made further observations on heather honey, finding that stirring decreased the viscosity as much as 200 fold. The unstirred gel form was found to have an apparent viscosity that increased rapidly as the stress applied in the measurement decreased. The same was true of the stirred sol form, although to a much lesser extent. In neither form was there found any evidence of a sharp elastic limit, "yield value". The smallest stress applied produced a noticeable deformation of the liquid. This author proposed "a semiquantitative measure of thixotropy". The method consists in "timing the fall of a steel ball through a sample of honey which has been left to stand overnight, disintegrating the gel by stirring with a perforated metal disk and then immediately timing a second ball of the same size."

Pryce-Jones (1936b) has made an extensive investigation of thixotropy in honey. His apparatus was of the concentric

cylinder type, the inner cylinder being suspended on a wire which carried a small mirror and two astatically arranged permanent magnets. Coils about these magnets could be energized to rotate the inner cylinder through a fixed angle. The return of the cylinder caused by the torsion of the wire was followed either by pencil or photographically, by the light reflected from the mirror. The curve that results is deflection of the cylinder plotted against time. The shearing force at any point on the curve is proportional to the deflection and the rate of shear is proportional to the slope of the curve. So far, Fryce-Jones has confined himself to a qualitative study of thixotropy, although the apparatus was designed for quantitative work.

A large number of samples have been examined by Fryce-Jones. All samples of Ling heather, Calluna vulgaris, were thixotropic and those from Bell heather, Erica cinerea, did not show the phenomenon. Manuka, Leptospermum scoparium, from New Zealand and an Australian honey 'Maleleuka' also gave evidence of a lesser thixotropy. Other honeys were non-thixotropic. The increase in viscosity, one minute after stirring could easily be recognized. This honey also developed a peculiar property, 'elastic-recoil', under the rapid shearing caused by the forced rotation of the cylinder. When the force was removed there was an immediate recoil of the cylinder against the force of torsion of the wire. The effect sometimes persisted for twenty-five minutes.

Pryce-Jones found a parallelism between the volume of protein precipitated by phosphotungstic acid and the thixotropic behaviour of the honey. Ling honey gave a precipitate of 30 cc. under the conditions of the determination while the corresponding treatment of clover or orange honey gave only 1 cc. of precipitate.

The removal of the colloidal material from ling honey entirely eliminated the thixotropy and elastic recoil. Addition of the ling colloids to a clover honey imparted these properties. The colloids from ling honey had an iso-electric point, and were precipitated by heating. Pryce-Jones concluded, therefore, that they were proteins.



## B. Discussion of Anomalous Viscosity

Before reviewing the evidence concerning the anomalous viscosity of honey, the general behaviour of materials subjected to a shearing stress may be discussed. If when the stress is removed, the strain disappears and the body regains the original shape, it is said to exhibit perfect elasticity. If the body is not perfectly elastic, it may exhibit various types of flow, of which three are designated as viscous, turbulent or plastic flow. Viscosity refers to the linear flow in which the amount of deformation is directly proportional to the deforming force, the viscosity being quantitatively expressed as the ratio of the deformation to the deforming force applied. As the deforming force is increased a point may be reached at which the above ratio suddenly decreases and the flow produced is called the turbulent flow. There may be cases where the ratio increases indefinitely when the deforming forces fall below a certain minimum, 'yield value', and this phenomenon is termed plastic flow. A fourth type of flow is that in which the deformation is not directly proportional to the deforming force and there may or may not be a 'yield value'. Eisenschitz (1933) discusses the subdivisions of this type. Glikman (1932) suggests the term 'thixotropic viscosity' for the anomalous viscosity of sols about to become gels.

The observations of Scott Blair (1935) on the anomalous

viscosity of heather honey have been substantiated by Pryce-Jones as mentioned above. Fulmer and Williams (1935) also have observed anomalous behaviour of honeys. Paine, Lothrop and Certler (1934) studied the viscous properties of buckwheat honey. They state, "viscosity values for buckwheat honey determined at high pressures were somewhat lower than values determined at lower pressures. This is apparently due to a slight plastic effect of the colloids, as the difference is much less for the ultrafiltered honey."

Barr (1931 p.5) has discussed the causes of anomalous viscosity and states that ".... discordances from the law of viscous flow have been observed at low rates of shear in the study of (i) very viscous liquids such as pitch, glass near its annealing temperature, or solutions of colophony in turpentine; (ii) colloidal solutions, particularly such as will set to a jelly when cooled to a lower temperature than that of the test or when used in high concentration; (iii) systems consisting of two liquid phases or of a solid and a liquid phase."

Many honeys are highly viscous and might be expected to behave in an anomalous manner as do the materials of group (1). Paine, Certler and Lothrop (1934), however, found that a pure sucrose solution of the same concentration did not show the anomalies they observed in buckwheat honey. Parks, Barton, Spaght and Richardson (1936) and Coumou (1935) have found con-

centrated dextrose solutions to behave as true solutions. Data presented in the present thesis show invert sugar solutions, Table 12, to behave as true fluids. The fact that honeys contain colloidal material causes them to fall in group (ii). There also exists the possibility that formation of a solid phase within the liquid, by granulation, may produce the condition as listed under group (iii).

The evidence points conclusively to the colloidal material in the honey as responsible for both thixotropy and anomalous viscosity. When the colloids are present, these effects are observed; when they are removed, or are present only in small amounts, thixotropy and anomalous viscosity are absent. It is therefore of interest to consider the chemical nature of the colloids. Pryce-Jones (1936b), as mentioned above, adduced evidence to show they were proteins. Paine, Gertler and Lothrop (1934) removed the colloidal material from a number of honeys by ultrafiltration and found it to be approximately half protein, the remainder being composed of beeswax, pento-  
sans, crude fiber and inorganic material. In the samples analyzed the concentration of the colloidal material varied from 0 to 1%. An heather honey, analyzed by Pryce-Jones (1936b), was found to contain 6% colloidal material.

An early proof of the presence of protein in honey was given by Thoni (1911) who employed the precipitin reaction to differentiate between true and spurious honeys. Many years

ago Chesire (1888) suggested a colloidal constituent as possibly responsible for the peculiar properties of heather honey, for "..... it becomes so gelatinous when ripened that the contents of a single cell, if successfully removed will retain its hexagonal figure for some time and this apparently from the presence of one or other of the pectose group of bodies..."

Before leaving the historical side of the problem it is of interest to review the viscometric studies that have been made on honey, aside from those mentioned. Fellenberg (1911) showed that the viscosity of a diluted sample of honey could be used to detect previous adulteration. Chataway (1932) gave tables for converting time of fall of a sphere in a standardized viscometer to the water content. Fulmer, Park and Williams (1935a) demonstrated the dependence of the rate of granulation on viscosity. Risga (1937) has discussed the variation of the viscosities of honeys with temperature in relation to the correct extracting temperature.

### III. EXPERIMENTAL

#### A. Method of Procedure

##### 1. Plan of Investigation

The experimental portion of the present research involved the determination of the apparent viscosities, at various rates of shear, of a number of honeys. As it was planned to attempt to find the relation between the thixotropy, the apparent viscosity and the chemical constitution of the honey, the water content, the nitrogen content and the calcium pectate number were determined.

##### 2. Experimental Methods

###### a. Choice of viscometer

The viscometer selected for the research had, as its first qualification, to be one in which viscosities might be determined at several rates of shear. Of the viscometers employed by previous investigators, that of Pryce-Jones (1936a) has been described above. Scott Blair (1935) worked briefly with the falling sphere viscometer, observing the effect on the apparent viscosity of using different sphere sizes. Since the use of this instrument involves a correction which is a function of the ratio of the radius of the sphere to that of the cylinder containing the medium, the different spheres were employed with different cylinders and the ratio was made the same in each case. This investigator also tested honeys in a plasto-

meter, that is, a capillary tube viscometer in which the driving pressure could be varied. This is substantially the instrument employed by Paine, Gertler and Lothrop (1934).

According to Barr (1931 p. 280), "the occurrence of a viscosity varying with the rate of shear may be detected in any of the instruments used for absolute determinations of viscosity in which provision is made for observations under different conditions, e. g. by changing the capillary or varying the pressure applied above the liquid in a capillary tube viscometer, or by varying the rate of rotation in a viscometer of the Couette type. The rate of shear may also be varied, when the viscosity is determined by means of the falling sphere, by using spheres of different diameters or density. The treatment in Lamb's Hydrodynamics (Art 339) shows that the maximum velocity gradient (at the equator) is  $1.5 v/r$  where  $v$  is the velocity of the sphere and  $r$  its radius." A number of instruments especially designed to detect anomalous behaviour in fluids are discussed by Barr (1931, pps. 281 to 290). Those that involve a capillary tube, such as the burette consistometer, Bingham's plastometer and the Hess viscometer were felt to be somewhat unsuited for the research because of the high viscosity of honey which would make times of extrusion large, and because of the tendency of small particles present in honey to clog the capillary. The Couette, or rotating cylinder type of apparatus is, according

to Barr (1931, p.281) suitable for detecting the effect of rate of shear on the apparent viscosity only on liquids not much more viscous than water, for ".....many systems such as the thixotropic sols investigated by Freundlich have a structure so sensitive to mechanical treatment that continued shear in a rotating cylinder apparatus may prevent or minimize its development."

It was decided to employ the falling sphere viscometer for the measurements desired. Since viscous anomalies had been detected in honeys by its use in these laboratories by Fulmer and Williams (1935), the further investigation of the phenomena with this instrument was felt to be a logical step. Furthermore the author had become interested in the development of the falling sphere viscometer for the study of anomalous systems in general.

The advantages of the falling sphere viscometer for the present work are as follows. The results are obtained directly in absolute units. The rate of shear and the shearing stress may be varied by changing the size of the sphere, its density, or the radius of the fall cylinder. Measurements involve a minimum of stirring effect, which is highly important in the study of a thixotropic substance. The observations may be made with an accuracy of 1%. This instrument served to determine both thixotropy, i. e., the difference in the viscosity of the stirred and unstirred honey, and anomalous viscosity

variable with the shearing stress.

In reply to Pryce-Jones' criticism mentioned above, of the falling sphere viscometer, along with all other types, for use in studying thixotropic substances, it should be stated that the instrument is employed here to obtain curves of apparent viscosity, or fluidity, against shearing force. From these curves comparisons between stirred and unstirred portions may be made at equal shearing forces. The unreproducibility of such a curve, which has been mentioned above, makes the following precautions necessary. Only three observations are made; the three spheres are of widely different sizes and the smaller, which give negligible stirring are used first. When such a procedure is followed it is felt that the falling sphere viscometer is an instrument well adapted to the study of thixotropic systems.



b. Previous use of the falling sphere viscometer in the study of anomalous fluids.

Phipps (1927) stated, "A number of rather thick liquids are not simply viscous, but plastic. This means that many measurements made on solutions of the above mentioned type with the falling sphere viscometer would have been different in value if another kind of sphere had been used. From this it appeared that it should be possible to obtain a plasticity curve with the falling sphere viscometer by using spheres of the same volume but different densities, or different volumes and the same or different densities."

"If the rate of fall of the sphere is plotted against  $d_2 - d_1$  where  $d_2$  is the density of the sphere and  $d_1$  that of the liquid, the curve obtained should show what type of liquid is being observed. If the result is a straight line passing through the origin, no plasticity will be shown. If the straight line intersects the x-axis at a point to the right of the origin, simple plasticity will be shown with a definite yield value and mobility. If the line passes through the origin but curves steadily upward, the sort of plasticity which is commonly observed in solutions of cellulose esters would be indicated."

If we calculate the maximum force exerted between any two layers of the liquid, or rather, the tangential force exerted on the walls of the sphere in a manner analogous to that used

by Bingham in calculating his force for capillary tubes, we would use the Stokes' law equation in the form  $F = 3/2 \frac{NV}{r}$ ,

where  $V$  is the velocity of the sphere and  $r$  its radius."

This "gives a curve which does not coincide with the one obtained with the Bingham and Murray plastometer. The reason for this discrepancy appears to be that in the falling sphere viscometer a larger fraction of the energy is dissipated in portions of the liquid where the shearing force is very small than in the case of the capillary tube viscometer. This makes the true viscosity-force curve somewhat more difficult to obtain than with the capillary-tube method, but does not mean that the instrument will be less valuable from a practical standpoint. Its usefulness lies in its ability to give information about the extreme lower portion of an ordinary plasticity curve, a portion which is very hard to investigate with other types of plastometers because of experimental difficulties, and also in the rapidity and ease of operation."

Kubo (1934) states, "In the descent of a sphere in a viscous liquid, the shearing force depends on the density of the sphere and also its radius. Phipps studied the first case, and now we have studied the second case, where the radius of the sphere is changed."

"We selected samples of rubber marked "First Latex Pale Crepe" which, after purification, we dissolved in Xylene. The concentrations of the two solutions were as follows:

(A) 3.83% and (B) 11.88%. "The viscous abnormality was measured by the velocity of fall of spheres of different diameters; the values were corrected for the influence of the ends and wall of the cylinder by the formulae of Ladenburg. From the results we determined the empirical relation between the velocity and radius of the sphere to be as follows, for solution (A)  $v = 3.18 r^{2.35}$  and for solution (B)  $v = 0.0956 r^{3.36}$ ." These equations have little value inasmuch as they comprise shearing force and the effect of this force on the apparent viscosity of a particular fluid.

De Waele (1931) made observations on the plasticity of celluloid solutions with the falling sphere viscometer, using the Lamb equation, mentioned by Phipps, to calculate the shearing force. He did not offer any evidence as to the validity of this equation. In his investigation the shearing force was varied by employing spheres of different sizes.

McBain and Watts (1932) devised a sphere viscometer in which the sphere was caused to traverse the fluid by centrifugal force. The rate of shear was varied by changing the centrifugal force and hence the velocity of the sphere. This apparatus and method may be criticised because of the fact that the fluid is subjected to a similar increase of force, which is likely to change its viscosity. In interpreting their results, the authors assumed the shearing force to be proportional to the centrifugal force and plotted apparent fluidities against the force in dynes. Pasynskiĭ and Rabinovich (1934)

have also employed centrifugal force to drive the sphere.

De Waele and Dinnis (1936) investigated the anomalous viscosity of nitrocellulose solutions with the falling sphere viscometer. These authors employed no equation for the calculation of the shearing force, but presented their results as apparent viscosity plotted against sphere radius. Speicher and Pfeiffer (1928) have also studied nitrocellulose solutions. Their results and those of De Waele and Dinnis have little importance in elucidating the theory of the instrument. It is very unfortunate that all of these authors have left their data in such a shape that recalculation is practically impossible.

Skrjabin (1936) has made measurements of the plastic properties of peat solutions by the method of the rising sphere. His work, which is rather inaccessible, is reviewed by Kulakoff (1937) and the details here given are from the latter author. A hollow wood or metal sphere was immersed to a measured depth in the peat solution with the aid of an especially designed tool, and allowed to go free. The time the sphere took to reach the surface was determined. The mass of the sphere and its effective density were varied by loading. Skrjabin modified the Stokes' equation to include the presence of a 'yield value' in the peat. The relations developed will be considered below.

Kulakoff criticised this work because of the super-Stokesian velocities and the approximate formulas employed.

In a comparison of the yield values and apparent viscosities found on the same peat solutions by the rising sphere, rotating cylinder, and capillary viscometers, he found approximate agreement between the last two methods and divergence between them and the first.

Brindle and Rowson (1936) demonstrated the relation between the suspending power of tragacanth solutions and the apparent viscosity as measured by the falling sphere viscometer. These authors state, "Viscosities of a mucilage prepared from gum sample A were determined by means of steel spheres of  $5/32$  inch,  $1/8$  inch and  $3/32$  inch diameter in the falling sphere viscometer, (the glass tube was 4.5 centimeters in diameter), using the smallest sphere first in order to minimize shearing action. The results show an increase in apparent viscosity of the same mucilage by decreasing the diameter of the sphere used, thus indicating that mucilage of tragacanth is a liquid of variable apparent viscosity. It is also obvious that the method of evaluation must be standardized in all details in order to yield the same results when used by different workers."

c. Theory of the falling

sphere viscometer.

The use of the falling sphere viscometer involves Stokes' law which may be formulated as follows, in terms of viscosity,

$$N = \frac{2}{9} \frac{(d_2 - d_1) 980r^2}{V} \quad (1)$$

In this equation,  $N$  is the viscosity;  $V$  is the velocity of fall of the sphere;  $d_1$  is the density of the medium;  $d_2$  is the density of the sphere;  $K$  is the acceleration due to gravity;  $R$  is the radius of the sphere. When the C. G. S. system is employed, the viscosity is expressed in terms of poises, the absolute unit of viscosity, that is dyne-sec/cm<sup>2</sup>. The above equation was derived on the basis of a number of assumptions. According to Arnold (1911) these are: (a) there is no slip between the medium and the surface of the sphere; (b) the discontinuities of the medium are small compared to the size of the sphere; (c) the sphere is rigid; (d) the velocity of fall is small; (e) the liquid is infinite in extent. One further assumption, implicit in the derivation, is that a perfect 'Newtonian' fluid is involved.

It is the conclusion of Bingham (1922, p. 35) that slip does not occur when the flow is linear. Lewin (1931) stated that when very small spheres are involved the slippage must be taken into account, but that this factor is not significant with sphere sizes commonly employed in the falling sphere

viscometer. It can be assumed, therefore, that significant slippage will not occur under the conditions of our observations. The requirement of rigid spheres is easily met by the use of ball bearings which are made in standard sizes with an accuracy of 0.001 inch or better. The requirement of low velocity of fall is almost automatically taken care of in work with honey, since the material is ordinarily highly viscous. The permissible velocity is more definitely defined by the following considerations. Mathematical theory has shown Stokes' law equation to be valid as long as the so-called Reynolds' number is negligible compared to unity. The Reynolds' number  $R_e$ , is defined as,

$$R_e = \frac{2Vr\eta g}{N} \quad (2)$$

The symbols in this equation have their previous meanings.

The requirement that the discontinuities of the fluid must be small compared to the size of the sphere is satisfied in honey. Each sample was prepared by heating to 60° for one hour, which dissolved all micro-crystals possibly present. Furthermore, the gel structure does not involve any discontinuity of a magnitude comparable to the smallest sphere employed. In support of this statement may be cited an experiment of Scott Blair (1935) in which an extremely small sphere was placed just under the surface of a sample of heather honey. The sphere was observed to fall at a steady rate.

That a perfect fluid is involved is not necessarily the case; and it is the aim of this research to characterize the honeys on the basis of their deviations from true fluidity. The procedure employed for this purpose may be advantageously discussed at this point. A perfect fluid obeys the following equation and is defined by it,

$$F = \eta \frac{dv}{dx} A \quad (3)$$

in which  $F$  is the force exerted by a plane of liquid of area  $A$  parallel to the direction of motion, when the velocity is increasing with the distance  $x$ , measured normally to the plane, at the rate  $\frac{dv}{dx}$ . At a given temperature in a perfect fluid, the factor  $\eta$  is constant. In an anomalous fluid this is not the case;  $\eta$  is a function of  $F$  or  $\frac{dv}{dx}$ . Viscometrists apply the equations derived for true fluids to these anomalous fluids, changing the meaning of  $\eta$  from viscosity to "apparent viscosity". This method is employed in the present paper.

The assumption that the fluid is infinite in extent cannot be fulfilled in the laboratory viscometer. The effect of the boundaries of the liquid is to make the sphere descend more slowly. If the simple Stokes' law equation is used to calculate viscosities from the rate of fall of a sphere in finite medium, high values will result. The viscosities calculated from the velocity of a sphere of radius  $r$  falling in a cylinder of radius  $R$  approach infinity as the ratio of  $r/R$  approaches



1. This effect has been termed 'wall effect' and will so be described in this paper. Ladenburg (1907) deduced that the top and bottom boundaries of the fluid should also exert a retarding influence on the descent of the sphere. This 'end effect' has been thought to be without practical significance by a number of viscometrists, while others have found it seemingly important.

A correction must be applied to reduce observed velocities to velocities in infinite medium so that the Stokes' equation may apply. The correction factor for a given viscometer and fixed  $r/R$  may be found, as was suggested by Gibson and Jacobs (1920) by calibration with a liquid of known viscosity. They gave the equation,

$$\frac{N_1}{N_2} = \frac{(d_2 - d_1) t_1}{(d_2 - d_3) t_2} \quad (4)$$

in which  $d_2$  is the density of the sphere,  $d_1$ , the density of the unknown liquid,  $d_3$ , the density of the calibrating liquid,  $N_2$ , its viscosity,  $N_1$ , the viscosity sought,  $t_2$ , the time of fall of the sphere over a given distance in the known liquid, and  $t_1$ , the time of fall in the unknown. In regard to this method Bingham (1922) states, "since there is a dearth of calibrating liquids of high viscosity, liquids are often chosen in which the velocity of fall is too great for strict application of Stokes' law." The above equation is not suitable for use in situations such as the present research in

which a variety of spheres and fall cylinders are employed.

Ladenburg (1907) deduced the following correction equation for the wall effect,

$$V(1 + 2.4 \frac{r}{R}) = V_{\infty} \quad (5)$$

in which  $V$  is the observed velocity and  $V_{\infty}$  is the velocity of fall in infinite medium. Lemin (1931) verified this equation for values of  $r/R$  up to 0.06, but found it entirely unreliable for higher values.

Ladenburg (1907) proposed a further equation to be used in conjunction with the wall correction. This was to correct for the end effect; the equation is,

$$V(1 + 3.3 \frac{r}{h}) = V_{\infty} \quad (6)$$

where  $h$  is the height of the column of liquid. If the sphere is timed over the middle 5/12 of the column, the factor is 3.3; if it is timed over the middle 4/5, the factor is 4.5. As mentioned above, there exists diversity of opinion regarding the validity of equation (6). Fulmer and Williams (1936) found that their results became more consistent with its use. Francis (1933) and Bacon (1936), however, were unable to detect any slowing of the sphere as it approached the end in the middle third of the tube.

The fact that Ladenburg's equation for the wall correction holds only for small values of  $r/R$  has made it of import-

ance to secure an equation to cover higher values. Sheppard (1917) proposed the relation,

$$T = T + \frac{C}{\left(\frac{R}{r} - 1\right)^2} \quad (7)$$

in which  $T$  is the observed time of fall,  $T$  the time of fall in infinite medium and  $C$  a constant for a particular size of sphere. The other symbols have their usual significance.

This equation was derived by consideration of data obtained from nitrocellulose solutions, which seems to have been an unfortunate choice; these solutions are known to show an apparent viscosity which is variable with the rate of shear. Barr (1931, p. 182), condemns equation (7) on this basis and states that "the conceptions leading to it appear to be unsound." Francis (1933) states that the equation does not hold for values of  $r/R$  larger than 0.33. It is extremely doubtful if it holds nearly that far. Fulmer and Williams (1936) found that the equation did not represent the observed variations of viscosity with  $r/R$  found by Lemin (1931) in his studies on glycerol.

Francis (1933) proposed two wall correction equations, both to be used without end correction. One, equation (9), was designed to apply to substances of low viscosity such as glycerol, and one, equation (10), to substances of high viscosity. In the following discussion,  $f_w$  is employed to represent the wall factor. The wall factor is defined by the

equation,

$$f_w = \frac{\mu_\infty}{\mu_s} \quad (8)$$

where  $\mu_s$  is the viscosity calculated by the use of the Stokes' equation with the correction for end effect made if it is to be employed, and  $\mu_\infty$  is the true viscosity of the fluid.

$$\frac{1}{f_w} = \left\{ \frac{(R - 0.475r)}{R - r} \right\}^4 \quad (9)$$

$$\frac{1}{f_w} = \frac{1}{\left(1 - \frac{r}{R}\right) 2.25} \quad (10)$$

Suge (1931) has proposed the relation,

$$\frac{1}{f_w} = \frac{1}{\left(1 - \frac{r}{R}\right) \frac{2.1}{1 - \left(\frac{r}{R}\right)^2}} \quad (11)$$

for values of  $r/R$  up to 0.371.

Fulmer and Williams (1936) advanced the empirical correction equation (12), which assumes the preliminary use of the Ladenburg end correction, equation (5),

$$\frac{1}{f_w} = (0.3)10^2 \cdot \frac{4}{R} + 0.7 \quad (12)$$

Derjagin and Wolarowitsch (1934) employed Ladenburg's wall and end correction equations for  $r/R$  values up to 0.1 and for larger values made interpolations from a table of experi-

mentally determined wall factors.

Foxen (1922) on theoretical grounds derived the equation,

$$f_w = 1 - 2.104\frac{r}{R} + 2.09\left(\frac{r}{R}\right)^3 - 0.95\left(\frac{r}{R}\right)^5 \quad (13)$$

Equation (13) was derived on the assumption that the velocity of fall is within the range where Stokes' law equation is valid and that the ball is descending in an infinitely long cylinder. No end correction is to be applied with this equation if the ball is timed over the middle 1/3 of the fall cylinder. Further assumptions involved are that  $Re^2$ ,  $Re\left(\frac{r}{R}\right)^2$ ,  $\left(\frac{r}{R}\right)^6$ , and  $Re^2\left(\frac{R}{r}\right)$  are negligible compared to unity. When this is not the case, the equation becomes more complicated.

It is evident that the above derivation is theoretical and it was not tested in actual practise by the author. The above work was largely overlooked until attention was called to it by Bacon (1936), who employed it in viscosity determinations in the range 10 to 10,000 poises.

The wall correction factors for various values of  $r/R$  given by the most valid of the foregoing equations are shown in table 1. The factor of the equation of Fulmer and Williams has the end correction from equation (6) multiplied into before it is used, which brings it into better agreement with the Faxen equation. Equation (8) is omitted from consideration since it is designed for substances less viscous than honey.

Table 1

Wall factors predicted by the various equations

r/R	Francis (High visc.) equation (10)	Suge equation (11)	Fulmer and Williams equation (12)	Faxen equation (13)
0.05	0.891		0.913	0.895
0.10	0.789	0.800	0.819	0.792
0.15	0.694		0.721	0.691
0.20	0.605	0.613	0.623	0.596
0.25	0.523		0.528	0.506
0.30	0.448	0.439	0.440	0.423
0.35	0.427		0.360	0.348
0.40	0.317	0.279	0.291	0.282
0.45	0.261		0.232	0.226
0.50	0.210	0.145	0.180	0.180

The various equations may be tested in part in the following manner. Taking the logarithm of both sides of  $f = \frac{N_{\infty}}{N_s}$

this equation becomes,

$$\log N_s = -\log f + \log N_{\infty} \quad (14)$$

In a given set of observations involving a perfect fluid,  $\log N$  is a constant, and a graph of  $\log N_s$  against  $\log f_w$  should result in a straight line with a slope of -1. The correct values of  $f_w$  will of course, satisfy these conditions.

For these tests the data of Bacon (1936) are employed since they deal, for the most part, with true fluids. While the data presented by Fulmer and Williams (1936) cover a wider range of values for  $r/R$ , they were obtained with anomalous fluids. With the exception of the two above sources, the viscosity data in the literature deal with very small values of  $r/R$ .

Table 2  
(Data from Bacon (1936))

"Silicate A, Tube A<sub>2</sub>"

Francis		Suge		Fulmer & Williams		Faxen		Ns	log Ns	% diff. between F. & W. & Faxen
$\frac{1}{f_w}$	$\frac{1}{\log f_w}$	$\frac{1}{f_w}$	$\frac{1}{\log f_w}$	$\frac{1}{f_w + e}$	$\frac{1}{\log f_w}$	$\frac{1}{f_w}$	$\frac{f}{R}$			
1.160	0.064	1.140	0.057	1.14	0.057	1.15	0.061	5309	3.725	+0.9
1.355	0.132	1.325	0.122	1.33	0.124	1.35	0.130	6224	3.794	+1.5
1.600	0.204	1.585	0.200	1.61	0.207	1.62	0.210	7431	3.8711	+0.6
1.920	0.283	1.950	0.290	1.99	0.299	1.98	0.297	9075	3.958	+0.5
2.335	0.366	2.400	0.380	2.52	0.401	2.50	0.398	11492	4.060	-0.8

Viscous Oil at 20°C

1.175	0.070	1.165	0.066	1.17	0.068	1.17	0.068	1510	3.179	±0.0
1.240	0.093	1.225	0.088	1.22	0.086	1.24	0.093	1597	3.203	+1.6
1.350	0.130	1.325	0.122	1.33	0.124	1.35	0.130	1740	3.240	+1.5
1.575	0.197	1.565	0.194	1.59	0.201	1.60	0.204	2056	3.313	-0.6
1.930	0.285	1.960	0.292	2.00	0.301	2.00	0.301	2574	3.411	±0.0

Colophony-turpentine (F. & W.)

(Data from F. & W. (1936))

1.17	0.069	1.17	0.068	1.17	0.068	0.074	75.3	1.877	±0.0
1.28	0.107	1.29	0.111	1.29	0.111	0.111	84.0	1.924	+0.8
1.42	0.153	1.42	0.154	1.42	0.147	0.147	95.9	1.982	±0.0
1.60	0.203	1.60	0.204	1.60	0.185	0.185	102.9	2.012	±0.0
1.71	0.234	1.75	0.243	1.75	0.215	0.215	115.7	2.603	+2.3
1.87	0.273	1.86	0.270	1.86	0.232	0.232	121.7	2.085	-0.6
2.23	0.348	2.25	0.353	2.25	0.288	0.288	150.5	2.177	+0.9
2.37	0.375	2.32	0.365	2.32	0.295	0.295	150.9	2.179	-2.0
4.12	0.615	4.06	0.609	4.06	0.433	0.433	274.7	2.439	-1.5



In constructing table 2, the wall factors given in table 1 were plotted and the appropriate factors for the particular values of  $r/R$  were read from the graph. As stated previously, the end correction was also made in employing the wall correction factor of Fulmer and Williams.

Table 3

<u>Material</u>	Slope			
	Francis	Suge	Fulmer and Williams	Faxen
Sodium silicate	-1.05	-1.04	-0.97	-1.00
Viscous Oil	-1.07	-1.05	-1.00	-1.00
Colophony turpentine (F. & W.)			-0.99	-0.97

When  $\log N_s$  was plotted against the values of  $\log \frac{1}{f_w}$  as given in table 2, the slopes indicated in table 3 were obtained. These results seem to indicate that the choice lies between the equation of Fulmer and Williams and that of Faxen, since the correct equation would give a line with a slope of one, as mentioned above.

It is instructive to compare the difference between the last named equations on a percentage basis; the difference will vary slightly according to the size of the cylinder. In the last columns of table 2 are given values for the percent

difference in the factors of Fulmer and Williams (with end correction) and of Faxen, assuming the former as reference.

This difference is slight and in comparing the viscous behaviour of honeys either equation would be equally satisfactory. Faxen's equation however has the advantage that a perfect fluid was involved in its theoretical derivation and its use permits the more definite recognition of such a fluid. For this reason the Faxen correction was applied in the present research.

In summary, the equation used was,

$$N = \frac{2}{9} \frac{(d_2 - d_1) 980r^2}{V} f_w \quad (15)$$

where  $f_w$  is the correction factor determined by equation (13).

d. Construction of the Viscometer

The fall cylinders were constructed of pyrex tubing selected for uniformity of inside diameter. The dimensions were taken with inside calipers, in several directions at the top and bottom of the tube. These measurements were averaged to obtain the inside radius  $R$  used in determining the wall correction. These and other pertinent data are given in Table 4.

Tube	Diameters (inches)		Table 4
	Top	Bottom	
No. 1	1.734	1.734	Average radius = 2.201 cms. Fall timed over 17 cms. Length of column = 40.2 cms.
	1.734	1.729	
	1.734	1.734	
No. 2	1.732	1.734	Average radius = 2.201 cms. Fall timed over 17 cms. Length of column = 40.2 cms.
	1.734	1.733	
	1.734	1.734	
No. 3	1.727	1.733	Average radius = 2.196 cms. Fall timed over 17 cms. Length of column = 40.2 cms.
	1.732	1.725	
	1.731	1.725	
No. 4	2.419	2.407	Average radius = 3.059 Fall timed over 14 cms. Length of column 33.6 cms.
	2.412	2.404	
	2.411	2.401	
No. 5	1.709	1.711	Average radius = 2.172 Fall timed over 14 cms. Length of column = 33.6 cms.
	1.711	1.708	
	1.708	1.711	
	1.706	1.714	
No. 6	0.738	0.736	Average radius = 0.936 Fall timed over 14 cms. Length of column = 33.6 cms.
	0.737	0.739	
	0.736	0.7375	
	0.738	0.736	

The timing lines were etched completely around each tube in a plane at right angles to its axis. A third line marked the level to which the liquid was poured. The bottom of each cylinder consisted of a turned brass base fixed to the glass with deKhotinsky or litharge-glycerol cement. The base fitted into a brass frame in the water bath. Figure I shows two fall cylinders in position in the thermostat. The motor stirrer, heating element, cooling coil and thermoregulator are not included in the diagram.

When a large number of observations are made on a given sample, the spheres pile up in the bottom of the fall cylinder and have the effect of shortening the column; they also tend to displace the timing interval from its symmetrical position. In an attempt to eliminate this effect, three cylinders were provided with bases that allowed spheres to be dropped into a reservoir after each determination. The construction of this special base is as follows. At the bottom of the column of liquid is an aperture which is covered during the descent of the sphere. The reservoir beneath the aperture consists of a brass cylindrical cup which fits snugly into the extended brass tube fitted to the fall cylinder. The cup locks into the brass frame when the tube is in the thermostat. When the fall cylinder is rotated from the top, a projection on the brass cup makes contact with, and removes, the cover from the aperture; when the projection is turned past the contact point a spring restores the cover to its former position.

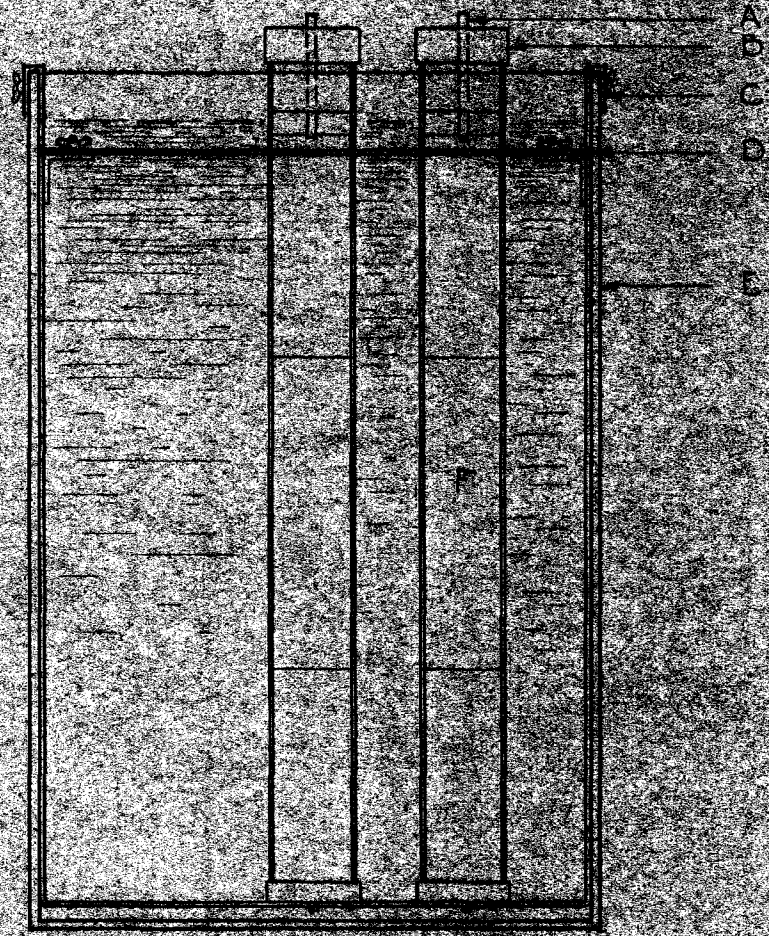
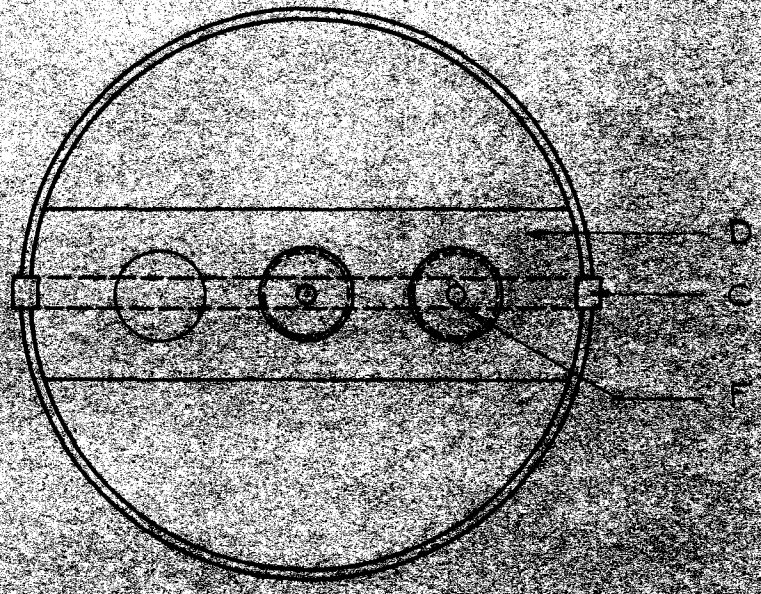


Figure 1.  
FALLING SPHERE VISCOMETER

After several tests, it is felt that in general, the advantages of this base are not great enough to offset the loss of tube length, and consequent loss in timing accuracy. For a cylinder of small radius in which large spheres are being employed the device is useful.

The spheres were released through a small glass tube which passed axially through a turned wooden cover at the top of the fall cylinder. This arrangement is shown in figure I. Several sizes of glass tubing were used to accommodate the different spheres. The tubing was placed to project slightly below the surface of the liquid. This caused the sphere to fall very slowly before entering the main body of the liquid, insuring that thermal equilibrium between the sphere and medium would be reached.

The spheres employed were ball bearings; in the run on Sweet Clover '33 these were of steel, while in the other determinations they were of stainless steel. Stainless steel spheres were found to give more consistent results after being employed several times, than did the steel spheres. The bearings were supplied in standard sizes with an accuracy of 0.001 inches or better; they were measured individually by micrometer calipers to 0.0001 inches.

The viscometer was contained in a large pyrex battery jar. A brass frame was built into this to hold the fall cylinders accurately vertical, as indicated in figure I. The jar was filled with distilled water and provided with a motor stirrer, cooling coil, heating unit and mercury thermoregu-

lator. At the fixed operating temperature a 'Red Top' thermoregulator manufactured by Hiergesell Bros. of Philadelphia was employed; this equipment held the temperature constant to  $\pm 0.02^{\circ}$ . For runs at different temperatures, an easily adjustable thermoregulator was designed; this is shown in Figure II. The space at g was filled with nitrogen. A platinum wire was sealed in at A and the screw device B for adjusting the level of the mercury in the capillary tube was cemented to the glass side arm. It should be emphasized that the external and internal screws must fit tightly to prevent mercury from working through. This thermoregulator held the temperature to  $\pm 0.03^{\circ}$ .

The temperatures were observed with a Beckmann thermometer reading to  $0.01^{\circ}$ . It was set by means of a thermometer which had been checked against a Bureau of Standards instrument.

The fall of the sphere was timed by means of a Gallet stopwatch which read to 0.1 seconds. The watch was checked over five minute intervals several times during the research.

Obtaining the absolute viscosity by Stokes' law equation involves a knowledge of the density of the liquid and the sphere. In determining the density of the honey, Babcock cream bottles were used as pycnometers. The difficulty in reading the meniscus made the densities obtained accurate only to  $\pm 0.002$ . The effect of the corrections involved in

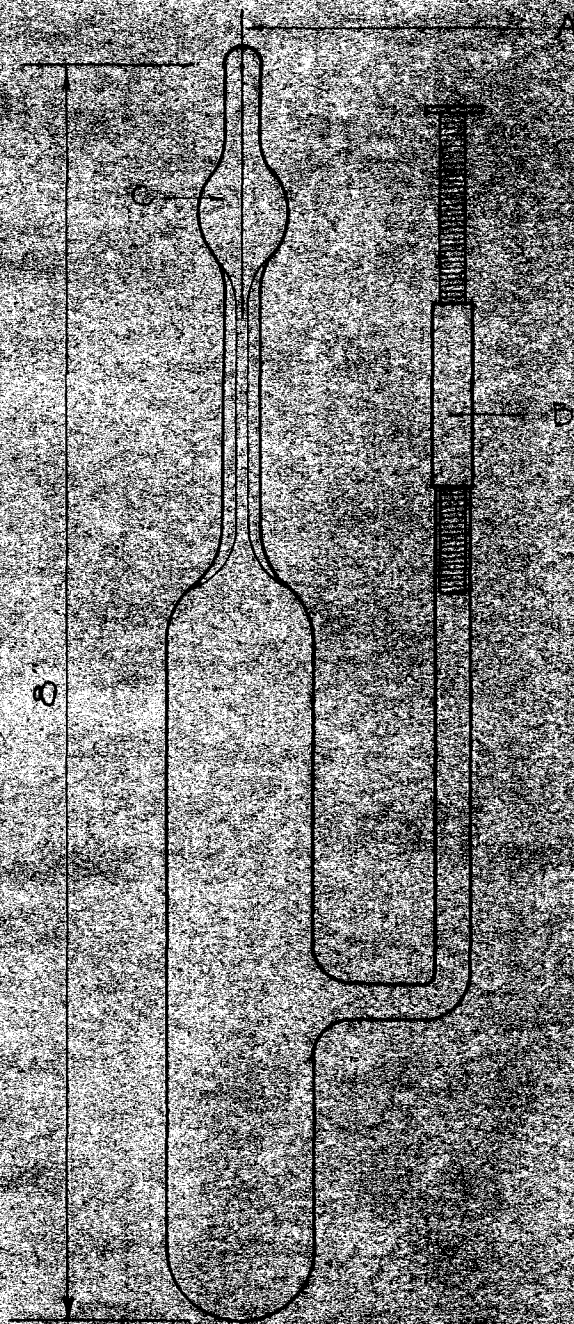


Figure 11.

THERMOREGULATOR



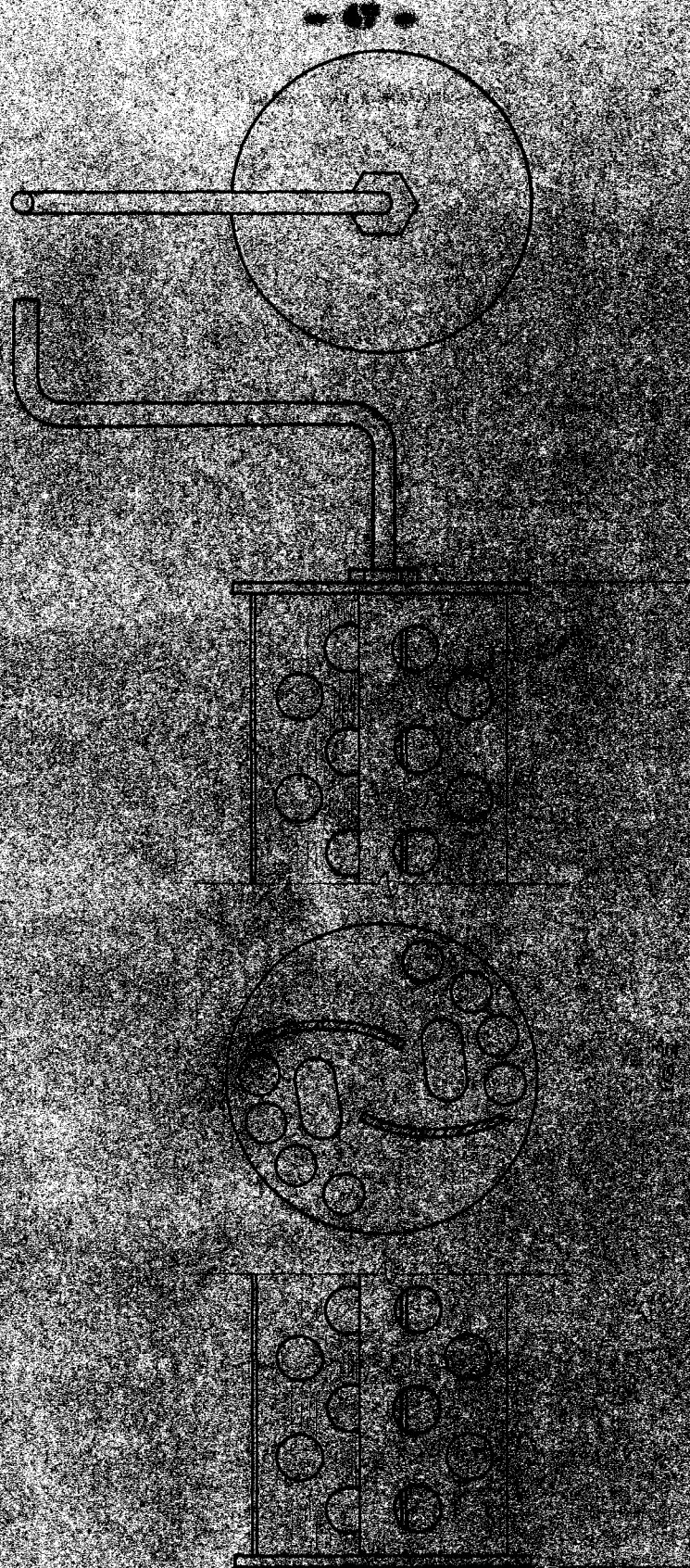
the various weighings for the buoyancy due to air fell within these limits; so the corrections were not made. The densities of the spheres were calculated from their weights and measured diameters. The three smallest sizes were weighed in groups of twenty spheres; the larger spheres were weighed individually. The principal error in this method, which is difficult to evaluate, is due to possible small deviation in perfect sphericity of the ball.

For small errors, the total differential of the corrected Stokes' equation may be used to determine the effect of the error in the various measurements on the calculated viscosity. Such a complicated form results however that the equation was not used. An approximation of the error to be expected in the viscosity may be obtained by calculations for typical cases. Since stopwatch readings are accurate to  $1/5$  of a second, the time of fall must not be less than 20 seconds if an accuracy of 1% is desired. With the other factors constant, an error of 0.01 units, which is larger than was involved, in the density term  $d_2 - d_1$ , when it has a value of 6.4 which is typical in honey determinations, will mean 0.2% error in the viscosity. An increment of 0.001 in the radius of a sphere of 0.2 centimeters radius means 1% error in the viscosity; for a sphere with a radius of 0.5 centimeters the value is 0.4%. The above values are for infinite medium. They would vary in finite medium according to the size of the sphere and cylinder. With the sphere and cylinder em-

ployed, the instrument error in the determinations ranged from 0.5% to 1.5%.

It happens that these errors are relatively minor compared to those due to bubble formation and eddy currents. Moreover when thixotropic materials are involved there is difficulty in obtaining check results due to the stirring action of the spheres. Lemin (1931) found that it was necessary to wait fifteen minutes between the passage of spheres to get consistent results even in a non-thixotropic medium.

The measurement of thixotropy involved the determination of the lowering in viscosity on stirring. DeBoer and Kruphorst (1932) devised a stirrer made up of a bundle of long straight rods, fastened at one end. The perforated plunger type of stirrer mentioned by Scott Blair (1935), was used and found to form a great many bubbles. A rotary stirrer was constructed and was found to give better results. A diagram of the stirrer is shown in Figure III. The perforated curved blades force the honey towards the center as the stirrer is rotated. For future work it is recommended that the area of the stirrer be less than that of the one employed in these studies, in order to cut down the amount of honey adhering when the stirrer is withdrawn.



ROTARY DRIER

e. Methods of Analysis

The water content of each honey was determined by the refractometric method developed by Fulmer, Bosch, Park and Buchanan (1934) The refractive index was determined by means of a Zeiss sugar refractometer. The corresponding water content was read from the table given by the above authors.

The relative pectin content of the honeys was determined by the method of Carré and Haynes (1922). This consists of hydrolyzing the pectins and pectinic acids in alkaline solution and then precipitating the highly insoluble calcium pectate by means of  $\text{CaCl}_2$  in the presence of acetic acid. The results are expressed as the 'calcium pectate number', i. e., grams of calcium pectate obtained from 100 grams of dry tissue or sample.

The above method involved acidification and boiling at the point in the procedure at which the calcium pectate is precipitated. Since this procedure would also precipitate protein material from the honey, which would be weighed as calcium pectate, the modification was introduced of acidifying, boiling and filtering before the alkaline hydrolysis.

Since oxalic acid might be present in the honey, it was necessary to consider that calcium oxalate would precipitate in the presence of acetic acid and would interfere with the analysis for pectin. According to Buston (1933) when oxalic acid is present the pectin solution is precipitated with

four times its volume of acidified absolute alcohol, allowed to stand overnight, filtered and washed with acidified alcohol and dissolved in warm water. The pectin is then determined as the calcium salt as before. No figures are available as to the accuracy of the determination. It is spoken of as 'entirely satisfactory' by Buston (1933). In view of the above possibilities, those honeys showing relatively large amounts of pectin by the ordinary analysis were re-analyzed by the method involving the alcohol precipitation. No oxalic acid was found.

The nitrogen content of the honeys was determined by the Kjeldahl method as given in Methods of Analysis, A. O. A. C. (1930). The volume of the precipitate which formed on treatment with phosphotungstic acid was determined by the method of Fryce-Jones (1936b). Five grams of the honey was diluted to 80 cc. and 20 cc. of a 2% solution of phosphotungstic acid was added. The solution was allowed to stand overnight and the volume of the precipitate read.

### 3. Materials and their preparation

Honey may be defined as the nectar and saccharine exudations of plants gathered, modified and stored in the comb by honey bees (Apis mellifera and Apis dorsata); it is laevorotatory, contains not more than 25% of water, not more than 0.26% ash and not more than 8% sucrose. Honey is named after the chief floral source from which they are derived.

Each sample of honey to be observed viscometrically was heated to 60° in a water bath and thoroughly stirred, to insure an homogenous sample. While at 60°, the honey was poured into the fall cylinders and specific gravity flasks; these were allowed to cool to room temperature and placed in the thermostat. The standard procedure in such cases as given by Barr (1931, p.291) is to "...heat the sample to a temperature at which there is no longer any viscometric evidence of structure, to cool it under definite conditions and then to maintain it at the temperature at which the test is to be made for a length of time sufficient to develop a uniform consistency." Since the size of the container affects the rate of setting of the thixotropic gel, a standard fall cylinder was employed.

## B. Results

The data obtained by methods developed during the course of this research are given in Tables 5 to 12. The viscosity and density values were determined at  $24.7^{\circ}$  unless otherwise noted and the refractive index readings at  $20^{\circ}$ . The following symbols are employed in the tables:  $C$  for the fall cylinder,  $R$  for the radius of the cylinder and  $r$  for the radius of the sphere which has a density  $d_2$ ;  $t$  represents the time of fall in seconds over the measured interval,  $N_s$ , the viscosity as calculated by the use of the uncorrected Stokes' equation and  $N_f$ , the corrected viscosity obtained by multiplying  $N_s$  by the wall factor  $f_w$ . The fall of the spheres was timed over 17 centimeters in fall cylinders 1, 2, and 3, and over 14 centimeters in cylinders 4, 5 and 6. This must be considered in comparing values in the  $t$  columns.

The discussion of this material is given in the next section.

Table 5

Sweet Clover Honey '36a

Density	= 1.436	Calcium pectate no.	= 0.016
Refractive index	= 1.5000	Volume of precipitate by method of Pryce-Jones	= 0.3 cc.
Water content	= 15.1%	Fall cylinders	
Nitrogen content	= 0.032%	No. 6	R = 0.936 = S
		No. 3	R = 2.196 = M
		No. 4	R = 3.059 = L

Honey stood 48 hours

C	r	d <sub>2</sub>	r/R	f <sub>w</sub>	t	N <sub>s</sub>	N <sub>f</sub>
S	0.0791	7.823	0.084	0.823	740.0	460.1	378.6
M	0.0791	7.823	0.036	0.925	798.0	408.8	378.1
L	0.0791	7.823	0.026	0.945	640.8	398.4	376.5
S	0.0791	7.823	0.084	0.823	741.2	460.8	379.3
M	0.0791	7.823	0.036	0.925	794.9	407.1	376.6
L	0.0791	7.823	0.026	0.945	645.8	401.5	379.4
L	0.0791	7.823	0.026	0.945	642.7	399.6	377.8
S	0.1981	7.816	0.212	0.574	165.6	644.9	370.2
M	0.1981	7.816	0.090	0.811	142.7	457.7	371.2
L	0.1981	7.816	0.065	0.864	111.9	435.7	376.4
S	0.1981	7.816	0.212	0.574	165.8	645.7	370.6
M	0.1981	7.816	0.090	0.811	142.7	457.7	371.2
L	0.1981	7.816	0.065	0.864	111.5	434.1	375.0
S	0.3171	7.787	0.339	0.364	99.3	986.1	359.0
M	0.3171	7.787	0.144	0.702	64.0	523.5	367.5
L	0.3171	7.787	0.104	0.785	47.6	472.7	371.1
S	0.3171	7.787	0.339	0.364	99.3	986.6	359.1
M	0.3171	7.787	0.144	0.702	64.0	523.5	367.5
L	0.3171	7.787	0.104	0.785	47.7	473.7	371.8

The same samples at 72 hours

S	0.0791	7.823	0.084	0.823	741.0	460.7	379.2
M	0.0791	7.823	0.036	0.925	801.4	410.5	379.7
M	0.0791	7.823	0.036	0.925	801.9	410.7	379.9
S	0.0791	7.823	0.084	0.823	735.6	457.3	376.4
L	0.0791	7.823	0.026	0.945	643.2	399.9	377.9
L	0.0791	7.823	0.026	0.945	643.2	399.9	377.9
S	0.0791	7.823	0.084	0.823	735.0	457.0	376.1
M	0.0791	7.823	0.036	0.925	802.3	410.9	380.1
S	0.1981	7.816	0.212	0.574	166.3	646.2	371.0
M	0.1981	7.816	0.090	0.811	144.0	461.8	374.5
L	0.1981	7.816	0.065	0.864	111.9	435.6	376.4



Table 5 (Concluded)

G	r	d <sub>2</sub>	r/R	f <sub>w</sub>	t	N <sub>B</sub>	N <sub>T</sub>
S	0.1981	7.816	0.212	0.574	164.4	631.9	367.4
M	0.1981	7.816	0.090	0.811	143.2	459.2	372.5
L	0.1981	7.816	0.065	0.854	111.7	434.9	375.7
S	0.1981	7.816	0.212	0.574	164.6	640.8	367.8
L	0.3171	7.787	0.104	0.785	47.7	474.0	372.1
M	0.3171	7.787	0.144	0.702	64.4	526.8	369.8
S	0.3171	7.787	0.339	0.364	98.9	982.1	357.5
M	0.3171	7.787	0.144	0.702	64.3	526.0	369.3
L	0.3171	7.787	0.104	0.785	47.6	473.2	370.5
S	0.3171	7.787	0.339	0.364	96.5	955.3	348.8
S	0.3171	7.787	0.339	0.364	96.8	961.3	349.9

The honey was stirred at this point

S	0.0791	7.823	0.084	0.823	722.9	449.5	369.9
L	0.0791	7.823	0.026	0.945	634.0	394.2	372.5
S	0.0791	7.823	0.084	0.823	720.2	447.8	368.5
M	0.0791	7.823	0.036	0.925	785.2	402.2	372.0
L	0.0791	7.823	0.026	0.945	637.4	396.3	374.5
M	0.0791	7.823	0.036	0.925	785.3	402.3	372.0
S	0.1981	7.816	0.212	0.574	162.4	617.9	354.7
M	0.1981	7.816	0.090	0.811	140.6	450.9	365.7
L	0.1981	7.816	0.065	0.864	109.6	426.7	368.7
S	0.1981	7.816	0.212	0.574	162.4	617.9	354.7
M	0.1981	7.816	0.090	0.811	140.6	450.9	365.7
L	0.1981	7.816	0.065	0.864	109.4	425.9	368.0
S	0.3171	7.787	0.339	0.364	100.0	993.1	360.4
M	0.3171	7.787	0.144	0.702	63.4	518.7	364.1
L	0.3171	7.787	0.104	0.785	46.4	460.8	361.7
S	0.3171	7.787	0.339	0.364	100.0	993.1	360.4
M	0.3171	7.787	0.144	0.702	63.3	517.8	363.5
L	0.3171	7.787	0.104	0.785	46.3	459.8	360.9

Table 8  
Sweet Clover Honey '36b

Density = 1.424      Volume of precipitate by  
 Refractive index = 1.4970      method of Pryce-Jones = 0.1cc.  
 Water content = 16.4%      Fall cylinders  
    No. 6      R = 0.936 = S  
    No. 2      R = 2.201 = M  
    No. 4      R = 3.059 = L

Honey stood 48 hours

C	r	d <sub>2</sub>	r/R	f <sub>w</sub>	t	M <sub>S</sub>	M <sub>f</sub>
S	0.1187	7.821	0.127	0.737	159.5	223.6	164.8
M	0.1187	7.821	0.054	0.888	161.6	186.6	165.7
L	0.1187	7.821	0.039	0.918	129.2	181.1	166.3
M	0.1187	7.821	0.054	0.888	161.8	166.8	165.9
L	0.1187	7.821	0.039	0.918	128.9	180.7	165.9
S	0.1187	7.821	0.127	0.737	159.2	223.1	164.5
S	0.1187	7.821	0.127	0.737	159.5	223.7	164.8
S	0.1981	7.816	0.212	0.574	73.0	284.8	163.4
M	0.1981	7.816	0.090	0.811	63.7	204.9	166.1
L	0.1981	7.816	0.065	0.864	50.3	196.4	169.7
S	0.1981	7.816	0.212	0.574	73.3	285.9	164.1
M	0.1981	7.816	0.090	0.811	64.0	205.6	166.8
L	0.1981	7.816	0.065	0.864	50.5	197.0	170.2
S	0.2775	7.779	0.428	0.428	49.4	376.1	161.2
M	0.2775	7.779	0.738	0.738	36.0	225.7	166.6
L	0.2775	7.779	0.811	0.811	27.5	209.3	169.7
S	0.2775	7.779	0.428	0.428	49.2	374.6	160.5
M	0.2775	7.779	0.738	0.738	36.0	225.7	166.6
L	0.2775	7.779	0.811	0.811	27.5	209.3	169.7
S	0.2775	7.779	0.428	0.428	49.2	374.6	160.5
M	0.2775	7.779	0.738	0.738	36.1	226.4	167.1
L	0.2775	7.779	0.811	0.811	27.5	209.3	169.7

Table 7  
Sweet Clover Honey '33

The measurements were made at 23.7°

Density	= 1.494	Calcium pectage no. = 0.011
Refractive index	= 1.4941	Volume of precipitate by method of Pryce-Jones = 0.1 cc.
Water content	= 17.5%	Fall cylinder No. 5
Nitrogen content	= 0.048%	R = 2.172 cms.

Honey stood 57 hours

r	d <sub>2</sub>	r/R	f <sub>w</sub>	t	N <sub>s</sub>	N <sub>f</sub>
0.0794	7.800	0.0365	0.9232	154.7	96.8	89.3
0.0794	7.800	0.0365	0.9232	154.9	96.9	89.4
0.1187	7.791	0.0547	0.8853	71.7	100.2	88.7
0.1584	7.785	0.0729	0.8474	41.85	104.0	88.1
0.3962	7.780	0.0912	0.8096	37.7	107.6	87.1
0.2380	7.799	0.1096	0.7721	20.2	113.6	87.7
0.2775	7.777	0.1278	0.7355	15.6	118.8	87.4
0.2776	7.771	0.1278	0.7354	15.4	117.3	86.3
0.3171	7.800	0.1460	0.6992	12.25	122.3	85.5
0.3568	7.790	0.1643	0.6635	10.25	129.4	85.9
0.3971	7.776	0.1829	0.6279	8.7	135.7	85.2
0.4361	7.772	0.2008	0.5941	7.7	144.8	86.0
0.4762	7.780	0.2193	0.5601	6.8	152.7	85.5
0.0794	7.800	0.0365	0.9232	53.7	96.1	88.8

The honey was stirred at this point

0.0794	7.800	0.0365	0.9232	148.4	92.8	85.7
0.1187	7.791	0.0547	0.8853	67.8	94.8	83.9
0.1584	7.785	0.0729	0.8474	40.1	99.6	84.4
0.1981	7.779	0.0912	0.8096	26.55	103.1	83.5
0.2380	7.821	0.1096	0.7721	19.3	108.9	84.1
0.2775	7.782	0.1278	0.7355	15.0	114.3	84.1
0.3171	7.819	0.1460	0.6992	12.0	120.2	84.0
0.3566	7.791	0.1642	0.6636	10.0	126.1	83.7
0.3971	7.773	0.1829	0.6279	8.65	134.9	84.7
0.4369	7.769	0.2012	0.5934	7.5	141.4	83.9
0.4762	7.783	0.2193	0.5601	6.6	148.2	83.0
0.0794	7.800	0.0365	0.9232	180.0	112.6	104.0
0.0794	7.800	0.0365	0.9232	180.75	113.1	104.4

Table 7 (Concluded)

$r$	$d_2$	$r/R$	$f_w$	$t$	$N_s$	$N_f$
0.1187	7.791	0.0547	0.8853	84.7	118.4	104.8
0.1187	7.791	0.0547	0.8853	85.3	119.2	105.6
0.1187	7.791	0.0547	0.8853	56.35	78.8	69.7
0.1584	7.785	0.0729	0.8474	33.75	83.8	71.1
0.1584	7.785	0.0729	0.8474	33.5	83.2	70.5
0.1981	7.792	0.0912	0.8096	22.05	85.8	69.5

Table 8

Holly Honey '31

Density	= 1.430	Calcium pectate no.	= 0.014%
Refractive index	= 1.4982	Volume of precipitate by method of Pryce-Jones	= 0.1 cc.
Water content	= 15.9%	Fall cylinder No.	1
Nitrogen content	= 0.035%	R	= 3.201 cms.

Honey stood 48 hours

r	d <sub>2</sub>	r/R	f <sub>w</sub>	t	N <sub>s</sub>	N <sub>f</sub>
0.1583	7.680	0.072	0.849	157.2	315.4	267.8
0.1583	7.680	0.072	0.849	157.6	316.2	268.4
0.3965	7.650	0.180	0.632	32.8	410.8	259.6
0.3965	7.650	0.180	0.632	32.6	408.4	258.1
0.1981	7.720	0.090	0.811	103.8	328.4	266.3
0.1981	7.720	0.090	0.811	102.3	323.5	262.3
0.1981	7.720	0.090	0.811	103.5	327.3	265.4
0.2378	7.683	1.108	0.775	75.1	340.2	263.6
0.2378	7.683	0.108	0.775	74.9	339.0	262.7
0.2774	7.682	0.126	0.739	57.6	355.2	262.5
0.2774	7.682	0.126	0.739	57.8	356.1	263.1
0.3171	7.682	0.141	0.709	46.2	372.1	263.8
0.3171	7.682	0.141	0.709	46.0	370.5	262.7
0.3570	7.621	0.162	0.667	38.0	384.1	256.2
0.3570	7.621	0.162	0.667	38.2	386.1	257.5
0.3965	7.650	0.180	0.632	32.2	403.3	254.9
0.3965	7.650	0.180	0.632	31.7	397.1	251.0
0.3965	7.650	0.180	0.632	32.0	400.8	253.3
0.3965	7.650	0.180	0.632	32.0	400.8	253.3
0.1583	7.680	0.072	0.849	154.5	309.9	263.1
0.1583	7.680	0.072	0.849	154.2	309.4	262.7
0.1583	7.680	0.072	0.849	155.3	311.6	264.5

The honey was stirred at this point

0.1583	7.680	0.0729	0.849	152.6	306.2	260.0
0.1583	7.680	0.072	0.849	153.2	307.3	260.9
0.2378	7.683	0.108	0.775	74.3	336.5	260.8
0.2378	7.683	0.108	0.775	74.1	335.6	260.1
0.3570	7.621	0.162	0.667	38.1	386.0	257.5
0.3570	7.621	0.162	0.667	37.8	382.1	254.9
0.3570	7.621	0.162	0.667	37.8	380.1	253.3
0.3570	7.621	0.162	0.667	37.8	382.1	254.9

Table 9

Tupelo Honey '31

Density	= 1.432	Calcium pectate no.	= 0.017
Refractive index	= 1.4986	Volume of precipitate by method of Pryce-Jones	= 0.3 cc.
Water content	= 15.7%	Fall cylinder No.	3
Nitrogen content	= 0.015%	R	= 2.196 cms.

Honey stood 48 hours

r	d <sub>2</sub>	r/R	f <sub>w</sub>	t	N <sub>s</sub>	N <sub>f</sub>
0.1583	7.680	0.072	0.850	157.0	314.9	267.6
0.1583	7.680	0.072	0.850	157.0	314.9	267.7
0.3965	7.650	0.181	0.632	33.0	413.2	261.1
0.3965	7.650	0.181	0.632	32.9	412.0	260.4
0.1981	7.720	0.090	0.811	103.2	326.4	264.7
0.1981	7.720	0.090	0.811	104.1	329.1	266.9
0.1981	7.720	0.090	0.811	104.5	330.3	267.9
0.2378	7.683	0.108	0.775	75.3	341.0	264.3
0.2378	7.683	0.108	0.775	74.6	338.0	262.0
0.2378	7.683	0.108	0.775	75.0	339.8	263.3
0.2774	7.682	0.126	0.738	57.3	353.0	260.5
0.2774	7.682	0.126	0.738	57.0	351.2	259.2
0.3171	7.682	0.144	0.702	45.3	364.7	256.0
0.3171	7.682	0.144	0.702	45.2	364.3	255.7
0.3570	7.621	0.163	0.666	38.0	384.0	255.7
0.3570	7.621	0.163	0.666	37.8	382.0	254.4
0.3570	7.621	0.163	0.666	37.6	379.9	253.0
0.3570	7.621	0.163	0.666	37.8	382.0	254.4
0.3965	7.650	0.181	0.632	31.7	397.0	250.9
0.3965	7.650	0.181	0.632	31.7	397.0	250.9
0.3965	7.650	0.181	0.632	31.7	397.0	250.9

The honey was stirred at this point

0.1583	7.680	0.072	0.850	154.3	309.4	263.0
0.1583	7.680	0.072	0.850	153.1	307.1	261.0
0.1583	7.680	0.072	0.850	154.3	309.5	263.1
0.2378	7.683	0.108	0.775	74.5	337.3	261.4
0.2378	7.683	0.108	0.775	74.4	336.9	261.1
0.3171	7.682	0.144	0.702	45.7	368.3	258.5
0.3171	7.682	0.144	0.702	45.6	357.1	257.7

Table 10

Sage Honey '33

Density	= 1.425	Calcium pectate no. = 0.111
Refractive index	= 1.4950	Volume of precipitate by method of Pryce-Jones = 0.1 cc.
Water content	= 17.2%	Fall cylinder No. 3
Nitrogen content	= 0.027%	R = 2.196 cms.

Honey stood 190 hours

r	d <sub>2</sub>	r/R	f <sub>w</sub>	t	N <sub>s</sub>	N <sub>r</sub>
0.1583	7.680	0.072	0.850	76.1	152.8	129.9
0.1583	7.680	0.072	0.850	76.0	152.7	129.8
0.3965	7.650	0.181	0.632	15.7	196.6	124.2
0.3965	7.650	0.181	0.632	15.7	196.6	124.2
0.1981	7.720	0.090	0.811	49.6	157.1	127.4
0.1981	7.720	0.090	0.811	49.6	157.1	127.4
0.2378	7.683	0.108	0.775	35.8	162.3	126.0
0.2378	7.683	0.108	0.775	35.9	162.6	126.0
0.2774	7.682	0.126	0.738	27.4	169.3	124.9
0.2774	7.682	0.126	0.738	27.4	169.7	125.2
0.3171	7.682	0.144	0.702	21.9	176.5	123.9
0.3171	7.682	0.144	0.702	21.7	174.9	122.8
0.3570	7.621	0.163	0.666	18.3	184.6	122.9
0.3570	7.621	0.163	0.666	17.9	181.1	120.6
0.3570	7.621	0.163	0.666	17.7	179.6	119.6
0.3570	7.621	0.163	0.666	18.2	184.1	122.6
0.3570	7.621	0.163	0.666	18.0	182.6	121.6
0.3965	7.650	0.181	0.632	15.2	191.2	120.8
0.3965	7.650	0.181	0.632	15.1	189.3	119.6

The honey was stirred at this point

0.1583	7.680	0.072	0.850	74.5	149.7	127.2
0.1583	7.680	0.072	0.850	74.1	148.8	126.4
0.1981	7.720	0.090	0.811	49.1	155.5	126.1
0.1981	7.720	0.090	0.811	49.0	155.1	125.8
0.2378	7.683	0.108	0.775	35.8	162.3	125.8
0.2378	7.683	0.108	0.775	35.7	161.8	125.4
0.2774	7.682	0.126	0.738	27.2	167.8	123.8
0.2772	7.682	0.126	0.738	27.2	168.0	124.0
0.3171	7.682	0.144	0.702	21.7	175.3	123.1
0.3171	7.682	0.144	0.702	21.5	173.3	121.6
0.3570	7.621	0.163	0.666	18.2	183.6	122.3
0.3570	7.621	0.163	0.666	18.1	183.1	121.9
0.3965	7.650	0.181	0.632	15.3	191.8	121.2
0.3965	7.650	0.181	0.632	15.2	190.6	120.5

Table 11  
Galberry Honey '33

Density = 1.409 Calcium pectate no. = 0.108  
 Refractive Index = 1.4900 Volume of precipitate by  
 method of Pryce-Jones = 0.1 cc.  
 Water content = 19.1% Fall cylinder No. 2  
 Nitrogen content = 0.049% R = 2.201 cms.

Honey stood 170 hours

r	d <sub>2</sub>	r/R	f <sub>w</sub>	t	N <sub>s</sub>	N <sub>f</sub>
0.1583	7.680	0.072	0.850	33.5	67.5	57.4
0.1583	7.680	0.072	0.850	33.5	67.5	57.4
0.3965	7.650	0.180	0.652	7.0	88.6	56.0
0.3965	7.650	0.180	0.652	7.0	88.6	56.0
0.1981	7.720	0.090	0.811	22.0	69.8	56.6
0.1981	7.720	0.090	0.811	22.0	69.8	56.6
0.2378	7.683	0.108	0.775	16.0	72.7	56.4
0.2378	7.683	0.108	0.775	15.9	72.3	56.0
0.2774	7.682	0.126	0.738	13.1	74.8	55.2
0.2774	7.682	0.126	0.738	12.0	74.2	54.7
0.3171	7.682	0.144	0.703	9.7	78.4	55.1
0.3171	7.682	0.144	0.703	9.7	78.0	54.8
0.1583	7.680	0.072	0.850	33.2	66.8	56.8

The honey was stirred at this point

0.1583	7.680	0.072	0.850	32.8	66.02	56.1
0.1583	7.680	0.072	0.850	33.3	67.03	57.0
0.1583	7.680	0.072	0.850	32.8	66.02	56.1
0.2378	7.683	0.108	0.775	15.8	71.8	55.6
0.2378	7.683	0.108	0.775	15.7	71.4	55.4
0.2774	7.682	0.126	0.738	12.0	74.4	54.9
0.2774	7.682	0.126	0.738	12.3	75.4	55.6
0.2774	7.682	0.126	0.738	12.1	75.1	55.4



Table 12

Invert Sugar at 23.7°

Density = 1.413 Nitrogen content = 0.00

Refractive index = 1.4919 Fall cylinder No. 2

R = 2.201 cms.

The solution stood 48 hours

r	d <sub>2</sub>	r/R	f <sub>w</sub>	t	N <sub>s</sub>	N <sub>f</sub>
0.1583	7.710	0.072	0.850	43.8	86.4	74.4
0.1583	7.710	0.072	0.850	43.4	87.7	75.5
0.1583	7.710	0.072	0.850	43.0	86.8	74.8
0.1981	7.720	0.090	0.811	38.7	91.0	75.0
0.1981	7.720	0.090	0.811	38.6	90.7	74.8
0.2378	7.680	0.108	0.775	20.8	94.4	74.4
0.2378	7.680	0.108	0.775	21.0	95.4	75.1
0.3171	7.680	0.144	0.703	12.9	104.2	75.1
0.3171	7.680	0.144	0.703	13.0	105.0	75.7

The solution was stirred at this point

0.2378	7.680	0.108	0.775	20.8	84.4	73.2
0.2774	7.680	0.126	0.738	16.1	99.5	73.4
0.3171	7.680	0.144	0.703	13.0	105.0	73.8
0.3971	7.650	0.180	0.632	9.1	117.0	73.9

#### IV. Discussion

Bingham (1922 p. 198-9) states, "The structures which may occur in colloidal solutions are of two kinds, which must be clearly differentiated from each other, because they give rise to phenomena which are in some respects exactly opposite, and this is true in spite of the fact that the two structures may in certain cases merge into each other."

"In the one case typified by gelatine, the structure requires time to form and the fluidity at a given moment depends upon the previous history of the solution. When moreover the solution is agitated by shaking or stirring or when it is heated, the structure is damaged and the fluidity is affected. This structure is similar in results to that which would be produced if an undercooled solution crystallized out in needleshaped crystals throughout the solution so that the flow of the resulting mass was stopped except by breaking the crystalline structure. Such a structure is a matter of slow growth, it may be partially destroyed by purely mechanical means, and it arises from forces which are of a polar nature. In view of this analogy we may speak of this type of structure as polar, whereas the second type is non-polar."

"In the second type of colloidal solution, typified by clay suspensions those forces are absent which bring about the setting of the gel. We have in the typical case merely

particles of suspended solid which affect to some extent the fluidity of the solution, but as we shall see the amount of lowering of the fluidity is very much less than when the structure is polar in character. If the distribution of the particles is uniform, the fluidity of the solution will be independent of time, agitation, and previous treatment."

The same author (1928) continues, "At first it was not recognized that there are quite distinct types of plastic flow but we must certainly recognize three types and there may be others."

"A suspension of finely divided solid in a very viscous medium affords an example of one type. Assuming the yield value to be the shearing stress required to start the continuous deformation, the amount of deformation has been found to be directly proportional to the excess of shearing stress, i. e.,

$$v = \mu (F - f)r \quad (16)$$

the mobility  $\mu$  being the analog of the fluidity."

Equation (16) represents the velocity relative to each other which two planes of liquid of unit area develop when the excess force  $F - f$  is applied to the one plane."

For liquids showing a yield value, Skrijabin (1936) employed a modification of Stokes' law equation which may be written,

$$N = \frac{2}{9} \frac{(d_2 - d_1 - \Delta)gr^2}{\nu} \quad (17)$$

where  $\Delta$  is a constant correction factor. This constant may be evaluated by making several velocity determinations with spheres of the same radius but different densities and extrapolating graphically to find the value of  $(d_2 - d_1)$  at zero velocity.  $\Delta$ , then, is the maximum difference between the density of the liquid and the sphere at which no motion takes place. According to Schischtschenko and Baklanow (1933) this constant bears approximately the following relation to the yield value  $f$ ,

$$f = \frac{g r \Delta}{3} \quad (18)$$

Kulakoff (1937) suggests that equation (18) gives a yield value which is too small because certain forces acting on the sphere were ignored in its derivation. He found the yield value obtained by application of equations (17) and (18) was smaller than those established by the use of the capillary and rotating cylinder viscometers. In our opinion, the method fails because the yield value is not considered in relation to the wall correction. At points in the fall cylinder where the shearing force is less than the yield value, flow will not take place. This will make the effective radius of the cylinder smaller than the actual radius.

Bingham (1928) states, "Polar colloids of the gelatin-in-water type certainly do not follow equation (16) and the difference seems to be not one of degree but to constitute a

different class entirely. .... there is given as an example a 1.71% solution of nitrocellulose in dibutylphthalate from measurements of Samuel Ellis. The reciprocal of the time of flow of 4 ml. of the solution is plotted against the shearing stress in dynes per square centimeter. The curve does not approach linearity at any shearing stress and it passes through the origin at finite slope. Various logarithmic formulas have been suggested for this type of flow such as  $v = aF^n$  by Wo. Ostwald and  $v = a(F - f)^n$  by W. Herschel. Neither of these equations, however, passes through the origin at a finite slope. An equation which has these properties, which seem to be characteristic of many colloidal solutions of this type, has been suggested by Dr. F. Williamson (private comm. to B),

$$v = aF + bF^n \quad (19)$$

and in a study of nitrocellulose solutions he found the value of  $n$  to be almost exactly 3.

Since  $v/F$  is proportional to the apparent fluidity  $\phi$  we may write the equation as,

$$\phi = a' + b'F \quad (20)$$

where  $a$  and  $b$  are constants. The former may be interpreted as the fluidity of the material at zero shearing stress and may be dependent upon the viscous flow of the medium through the micellian structure."

The extensive quotations are made here from Bingham because the viscometric studies of honey indicate that it is

of the polar type of colloid. This is to be expected from the analyses of Paine, Gertler and Lothrop (1934), mentioned above, in which approximately half of the colloid material from a number of honeys was found to be protein.

Bingham (1928) has further valuable material to offer. "The parameters a and b of equation (20) appear to be independent of the dimensions of the instrument used in their determination. Mr. Wiggam has found the equation to apply to solutions in some ten solvents of as many types of nitro-cellulose."

In applying equation (20) in the present research it is necessary to know the shearing force applied by the sphere. According to Phipps (1928), "If we calculate the maximum shearing force exerted between two layers of liquid, or rather, the tangential force exerted on the walls of the sphere in a manner analogous to that used by Bingham in calculating his F for capillary tubes ( $F = P r/2L$  where P is the pressure in dynes, r the radius, and L the length of the capillary), we would use the Stokes' law equation in the form,

$$F = (3/2) \frac{\eta V}{r} \quad (21)$$

where the symbols have their usual meanings."

As mentioned above, Phipps found that equation (21) did not produce, when applied to data from the falling sphere viscometer, a viscosity-shearing force curve continuous with

that from the Bingham-Murray plastometer. This was to be expected, since equation (21) is approximate for a number of reasons, and at best does not give a value of  $F$  comparable to that employed by Bingham and Murray. The equation was developed by Lamb (1924) to give the maximum shearing force, at the equator of the sphere. A true fluid was assumed in its derivation, as was infinite medium; neither of these conditions are met in the work of Phipps or in the present research. The value for  $\underline{N}$  substituted in it is apparent viscosity, which is a function not only of the maximum rate of shear at the equator of the sphere, but more directly of the average rate of shear throughout the liquid. Bingham's relation,  $P_r/2L$ , on the other hand, is the maximum force per unit area at the walls of the capillary. The apparent viscosity calculated from observations with the Bingham-Murray plastometer depends on the average rate of shear throughout the liquid. It is apparent that the maximum shearing forces, maximum rates of shear and average rates of shear are not necessarily the same from one instrument to the other. That the two methods should give divergent results is not proof that one of them is false.

A serious objection to equation (21) comes from a consideration of our observations on an honey, Sweet Clover '36a (see Table 5). Substituting from the corrected Stokes' equation, equations (21) becomes,

$$\underline{F} = 1/3 (d_2 - d_1) r f_w \quad (22)$$

In the data of Table 5, the term  $(d_2 - d_1)$  is practically constant and the shearing force, according to equation (22), is proportional to the product  $\underline{r}f_w$ . In Figure IV the apparent viscosities for the honey, observed with three sizes of spheres in three fall cylinders of different radii, are shown plotted against  $\underline{r}f_w$ ; the values are taken from Table 12. The large decrease in viscosity observed in the smallest cylinder demonstrates that the effective shearing force is greatest there; the expression for the shearing force, equation (22), however, gives lower shearing force values for the observations in the small cylinder than for those in the large cylinder.

Pasynskii and Rabinovich (1934) have investigated anomalous systems with the falling sphere viscometer. They state, "An important part of the determination of the structural viscosity of colloidal solutions by the means of the falling sphere method is the determination of the corresponding velocity gradients. The calculation of the velocity gradients here was based on the assumption that the velocity distribution in the liquid due to the fall of the sphere was in the shape of a truncated cone." This is shown in Figure V. "Consequently the velocity gradient will be characterized by the relation of the height of the truncated cone to the difference in the radii of the cylinder and



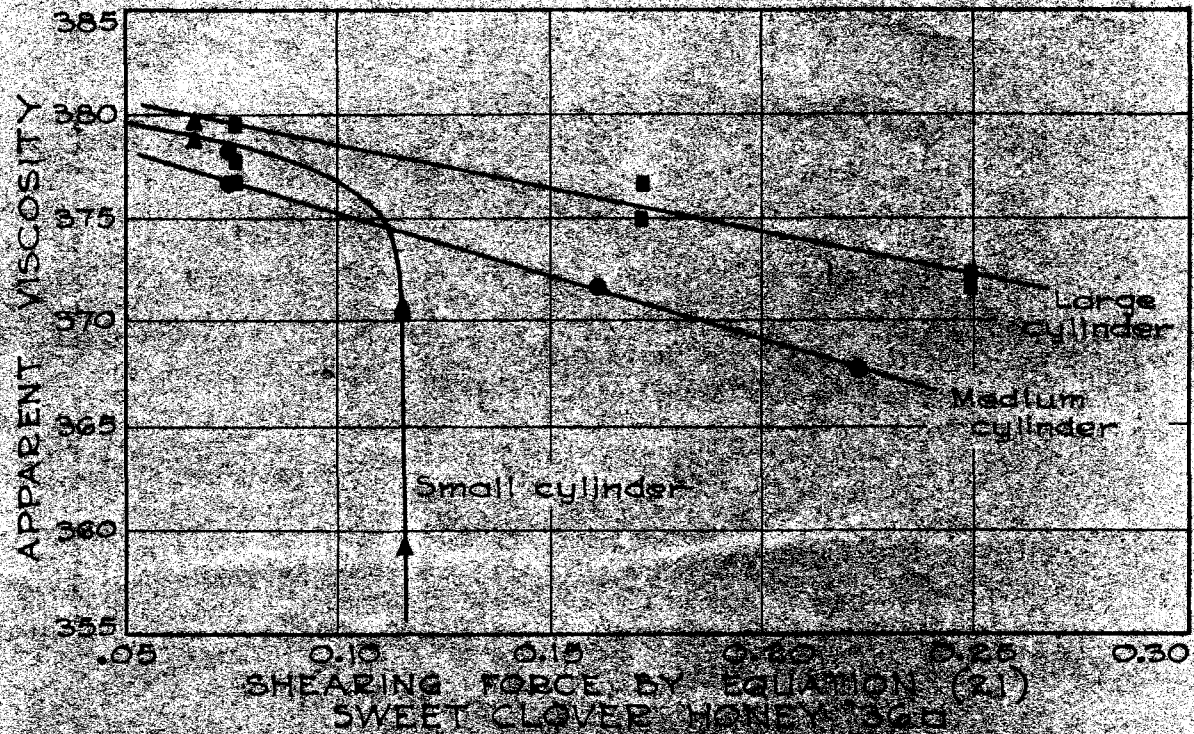


Figure IV. A Test of the Luck Equation for Shearing Force in the Falling Sphere Viscometer.

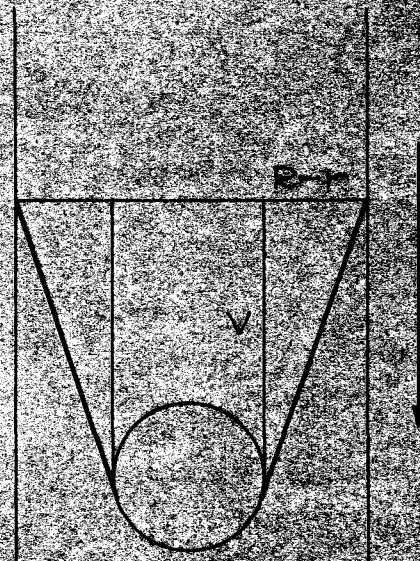


Figure V. The Velocity Gradient in the Falling Sphere Viscometer according to Poiseuille and Hagenbach.

sphere. The height of the truncated cone is  $V = \frac{D}{t}$ , where  $D$  is the distance in centimeters traveled by the sphere in  $t$  seconds. Consequently from the figure, the velocity gradient  $\frac{dV}{dx}$  is given by the equation,

$$\frac{dV}{dx} = \frac{V}{R - N} = \frac{D}{(R - r)t} \quad (23)$$

In nitrocellulose solutions higher values of the viscosity are obtained by the falling ball than by the capillary viscometer, yet it is possible to project data from both instruments on a common curve by disposing points according to their velocity gradients. It follows that the main difference between the two types of viscometers consists in differing velocity gradients and that under rational interpretation of the data the two methods give like results even though the values of viscosity obtained vary greatly."

The shearing force at the equator of the sphere may be obtained from the equation of Pasynskiĭ and Rabinovich by multiplying it by the apparent viscosity.

$$F = \frac{ND}{(R-r)t} \quad (24)$$

The assumption of these authors that the velocity gradient varies according to their diagram is questionable. The actual distribution of the velocity gradient in each anomalous fluid must be determined by experiment. The methods by which this may be done are discussed by Richardson (1935)

When equation (24) is applied to the data of Phipps (1928), the shearing force-viscosity curve becomes continuous with that from the Bingham-Murray plastometer. This agrees with the observations of Pasyanskiĭ and Rabinovich. In the light of the above discussion, the agreement is interesting, but not necessarily proof of the validity of equations (23) and (24).

When the apparent viscosity of the Sweet Clover '36a is plotted against the shearing force, as calculated by equation (24), it is found that the observations in the small cylinder are correctly placed at high shearing values. Furthermore, the data from all three cylinders fall reasonably well on a continuous line. This is shown in Figure VI; the data are from Table 13.

A possible effect that must be considered here is the tendency for the thixotropic setting to be most rapid in the smaller vessel. Since, however, the viscosities obtained at the lowest rates of shear, i. e., with the smallest spheres are approximately the same, it may be assumed that nearly the same setting has occurred in each cylinder.

The presumption seems to be, from this evidence, that equation (24) is essentially correct. It should be emphasized, however, that honey is a fluid definitely unsuited to check such an equation. In addition to the setting of this gel, which proceeds at different rates in the different

Table 13

Sweet Clover \*36a (see page 52 for complete presentation)

Tube	$\underline{I}$	$\underline{f} \times \underline{I}$	$\underline{N}$	$\frac{NV}{R - r}$	Fluidity $\times 10^{-3}$
6	0.079	0.065	378.6	8.764	2.641
3	0.079	0.073	378.1	3.877	2.644
4	0.079	0.075	376.5	2.797	2.656
6	0.079	0.065	379.3	8.766	2.636
3	0.079	0.073	376.6	3.877	2.656
4	0.079	0.075	379.4	2.797	2.636
4	0.079	0.075	377.6	2.797	2.648
6	0.198	0.114	370.2	42.41	2.701
3	0.198	0.160	371.2	22.65	2.694
4	0.198	0.171	376.4	16.46	2.657
6	0.198	0.114	370.6	42.41	2.698
3	0.198	0.160	371.2	22.65	2.694
4	0.198	0.171	375.0	16.46	2.666
6	0.317	0.115	359.0	76.86	2.786
3	0.317	0.222	367.5	50.88	2.721
4	0.317	0.249	371.1	39.24	2.695
6	0.317	0.115	359.1	76.85	2.785
3	0.317	0.222	367.5	50.88	2.721
4	0.317	0.249	371.8	39.23	2.69



Figure 11. A test of the proposed relationship Equation (24) for Shearing Force in the Sweet Clover Honey Solution.

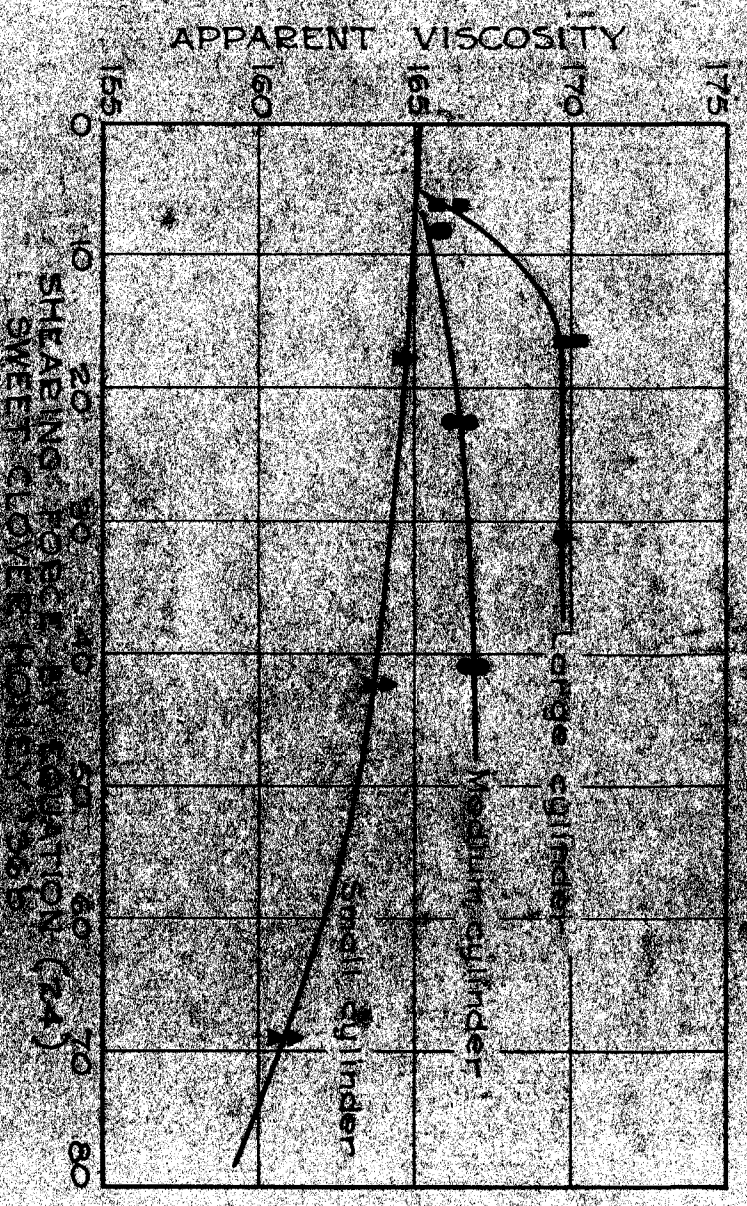


Figure 11. A test of the proposed relationship Equation (24) for Shearing Force in the Sweet Clover Honey Solution.

cylinders, there is the interfering property of 'elastic-recoil' observed by Pryce-Jones (1936). For example, in Figure VII the shearing force-apparent viscosity curve is constructed for Sweet Clover '36a, using equation (24) to calculate the shearing force; the data are given in Table 14. Here, evidently the tendency for the apparent viscosity of the honey to decrease with increasing shearing force has superimposed on it an extra resistance to the passage of the sphere increasing according to its size and that of the fall cylinder. This seems to be elastic-recoil as far as such a property can be identified in a different instrument. It will be so termed in the following discussion.

In testing the validity of equations (21) and (24) for calculating the shearing force, observations on fluids showing only the property of viscosity variable with the rate of shear are needed. These observations should be made with various sizes of spheres and fall cylinders. The data of Pasynskii and Rabinovich (1934), Phipps (1928), Speicher and Pfeiffer (1928), McBain and Watts (1932), De Waele (1931), De Waele and Dinnis (1936) and Hirata and Kubo (1934) are unsuitable for the reason that either the sphere or cylinder size was held constant. The data of Sheppard (1917) seem to be the best available for test purposes although the observations with the largest sphere do not satisfy the Faxen conditions. This investigator made

Table 14  
Sweet Clover Honey '36b

N	$\frac{NV}{R - r}$	Fluidity x 10 <sup>-3</sup>
S 164.8	17.7	6.07
M 165.7	8.391	6.03
L 166.3	6.128	6.01
S 164.5	17.7	6.08
M 165.9	8.391	6.03
L 165.9	6.128	6.03
S 164.8	17.7	6.07
S 163.4	42.47	6.12
M 168.1	22.68	6.02
L 169.7	16.50	5.90
S 164.1	42.48	6.09
M 166.8	22.69	5.99
L 170.2	16.5	5.87
S 161.2	69.33	6.20
M 166.6	41.01	6.00
L 169.7	31.06	5.89
S 160.5	69.31	6.23
M 167.1	41.0	5.98
L 169.7	31.00	5.89

observations on nitrocellulose solutions with a variety of spheres and cylinders. Unfortunately, certain of the results were not included, and in utilizing this work, indirect methods must be employed. The Stokes-Faxen equation,

$$N = \frac{2}{9} \frac{(d_2 - d_1) g r^2 t f w}{D} \quad (25)$$

shows that for a series of spheres of the same density, a given liquid, and a given distance of fall, the apparent viscosity is expressed by the following equation,

$$N = R r^2 t f w \quad (26)$$

This equation is the most convenient for the consideration of Sheppard's results. In Figure VIII,  $r^2 t f w$  is plotted against the shearing force as calculated by the modified equation of Lamb-Phipps, equation (22). In Figure IX the same expression is plotted against the shearing force calculated by the equation of Pasynskii and Rabinovich. For convenience this has been expressed,

$$\frac{N V}{R - r} = \frac{\frac{2}{9} (d_2 - d_1) g r^2 f w}{R - r} = \frac{r^2 f w}{R - r} \quad (27)$$

The data for both figures are given in Table 15.

From the figures it is evident that the equation of Pasynskii and Rabinovich is valid while that of Lamb is not.

It is now possible to find if the Williamson-Bingham relation, equation (20), applies to honey. It is at once apparent that the value of the constant  $a$ , which represents the fluidity at zero shearing force, will depend on the size



Table 15

A Nitrocellulose Solution

Sheppard's Data

Fall distance = 19.5 cms.

$I = 0.3170$

r/R	$f_w$	t	$f_w t R^2$	$f_w t$	$\frac{I^2 f_w}{R - I}$
0.33	0.375	110.5	4.16	0.119	0.0594
0.25	0.506	75.0	3.81	0.160	0.0535
0.20	0.596	63.6	3.81	0.189	0.0473
0.16	0.673	57.2	3.87	0.213	0.0427
0.14	0.710	53.1	3.79	0.225	0.0375
0.13	0.730	51.0	3.74	0.231	0.0331
0.11	0.772	50.1	3.89	0.244	0.0306
0.10	0.792	49.5	3.94	0.251	0.0279
0.091	0.810	48.9	3.98	0.257	0.0257
0.085	0.826	48.2	4.00	0.262	0.0238
0.077	0.840	47.8	4.03	0.266	0.0222

$I = 0.4762$

0.33	0.375	38.2	3.25	0.169	0.094
0.25	0.506	29.4	3.38	0.241	0.0804
0.20	0.596	25.1	3.39	0.284	0.0709
0.16	0.673	23.2	3.54	0.329	0.0641
0.14	0.710	22.0	3.54	0.338	0.0564
0.13	0.730	21.1	3.49	0.348	0.0497
0.11	0.772	20.9	3.66	0.368	0.046
0.10	0.792	20.4	3.66	0.377	0.046
0.091	0.810	20.6	3.78	0.386	0.0386
0.083	0.826	20.5	3.84	0.393	0.0358
0.077	0.840	20.4	3.89	0.400	0.0308

$I = 0.635$

0.33	0.375	23.1	3.49	0.238	0.119
0.25	0.506	16.2	3.31	0.321	0.107
0.20	0.596	13.1	3.15	0.378	0.0946
0.16	0.673	12.0	3.26	0.427	0.0855
0.14	0.710	11.9	3.41	0.451	0.0752
0.13	0.730	11.8	3.47	0.464	0.0662
0.11	0.772	11.6	3.61	0.480	0.0613
0.10	0.792	11.4	3.64	0.503	0.0559
0.083	0.826	11.2	3.73	0.524	0.0477
0.077	0.840	11.1	3.76	0.534	0.0444

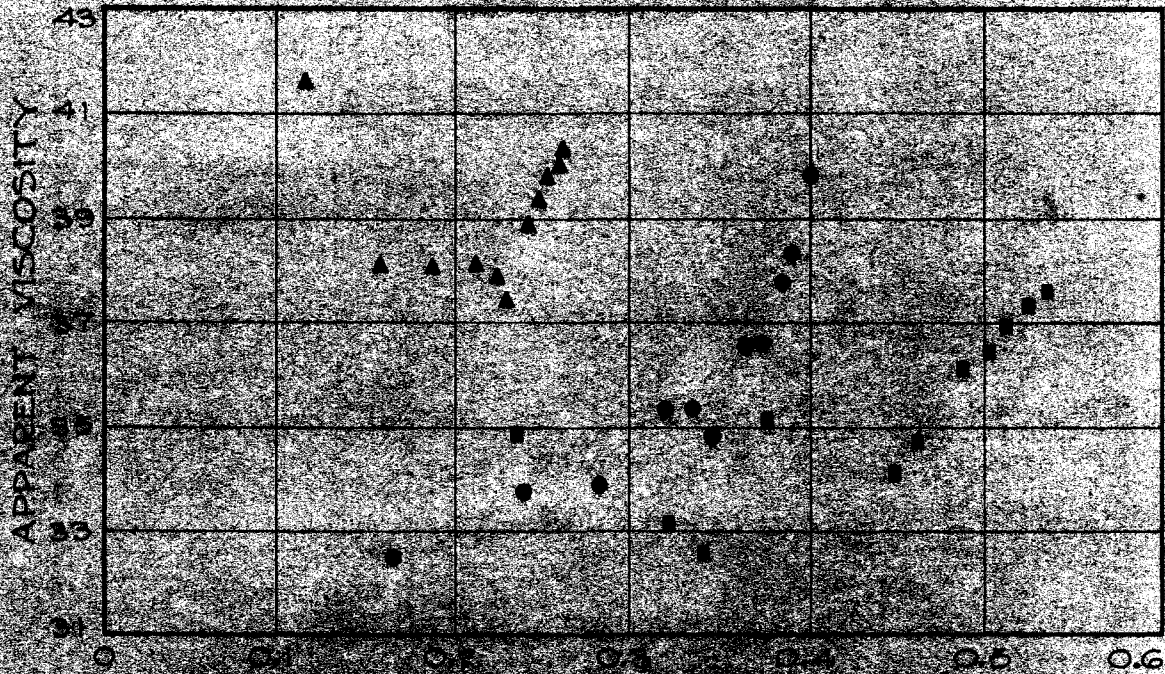


Figure 12. Shearing Rate by Equation (21) for a Nitrocellulose Solution. Data from Sheppard Figure 11, a part of the data collection.

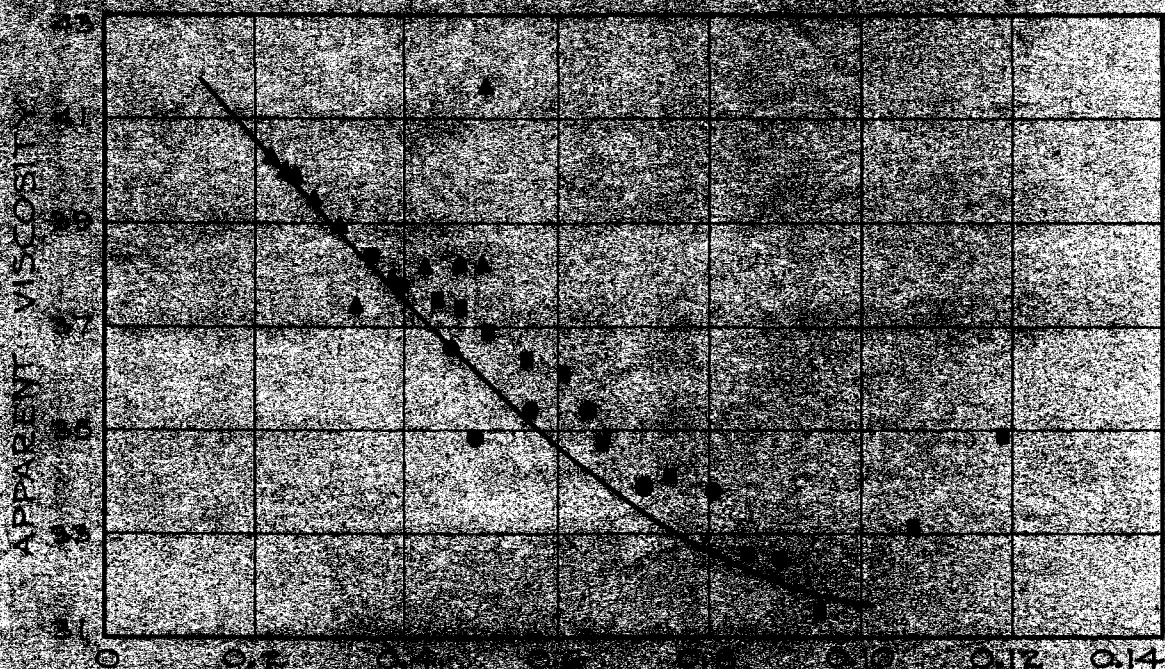


Figure 13. Shearing Rate by Equation (24) for a Nitrocellulose Solution. Data from Sheppard Figure 11, a part of the data collection.

of the containing vessel when a thixotropic material is involved. In Figure X, the fluidity of Sweet Clover '36a, which is practically non-thixotropic, is shown plotted against the shearing force. The data for the curve are taken from Table 13. It is evident that the straight line predicted by equation (20) is obtained for low shearing forces and that not only values of a, but also those of b, the slope, are influenced by the size of the vessel.

The same graph constructed for Sweet Clover '36b, Figure XI, shows a separate curve for each cylinder; only one of the curves apparently obeys the equation; the data are from Table 14. Equation (20) then, seems definitely not to apply to all honeys.

Over short shearing force intervals these curves, as well as the viscosity-shearing force curves, approximate straight lines. The slope of the curve at a standard reference point, for example, at zero shearing force, suggests itself as a measure of the deviation of the honey from true fluidity. A true fluid, of course, would show a slope of zero. The property of elastic recoil, however, interferes with this method of rating. The fluidity-shearing force curve of Sweet Clover '36b for the small cylinder, Figure XI, demonstrates the tendency of the fluidity of this honey to increase in value as the shearing force is increased. This tendency is seen to be masked in the larger cylinders,

Figure 11. The change of fluidity with shear rate.

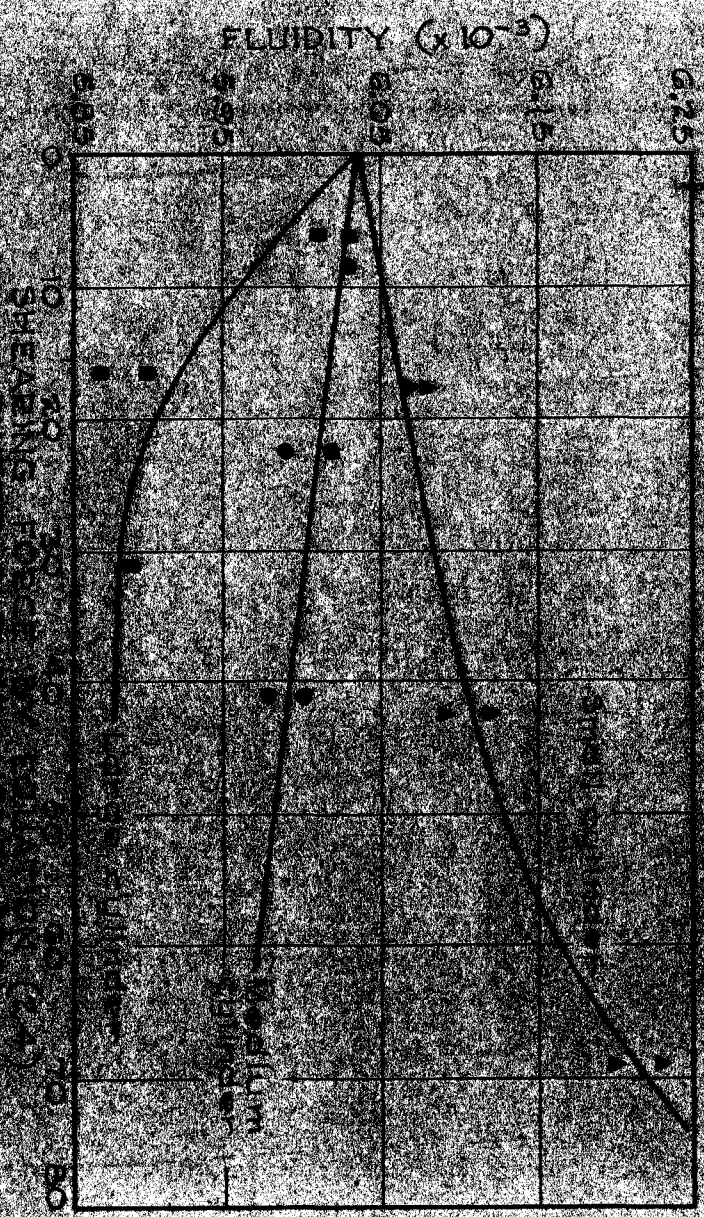
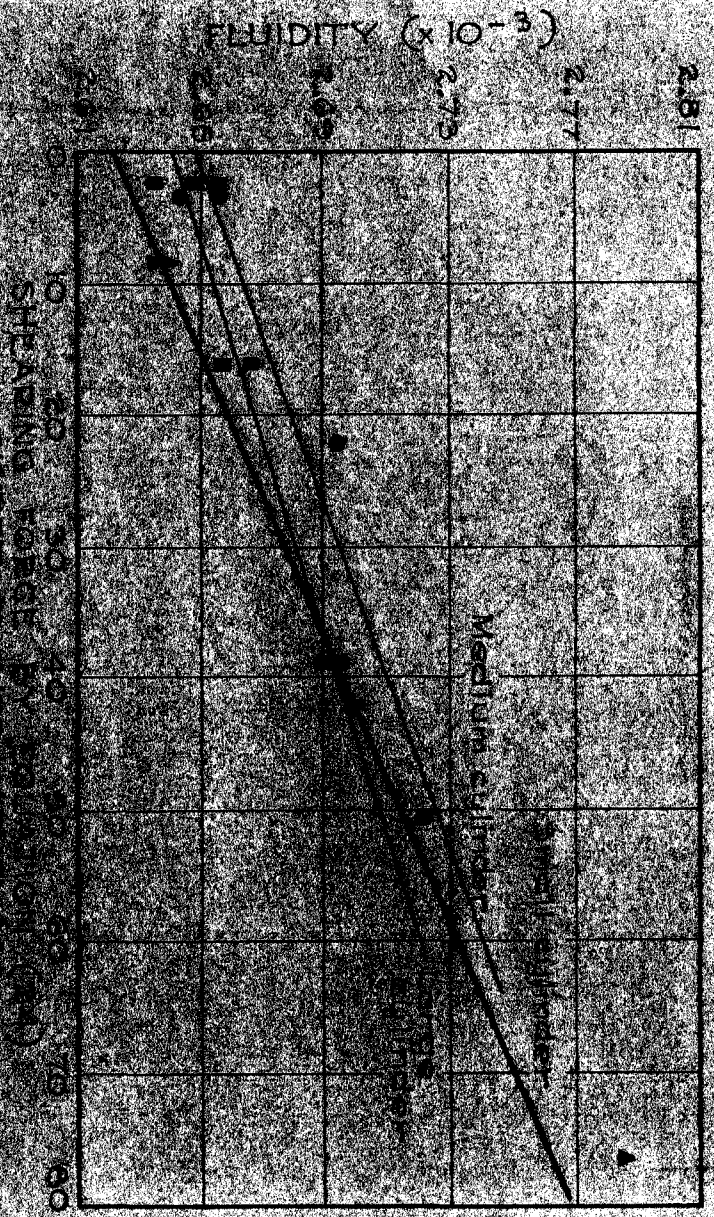


Figure 12. The change of fluidity with shear rate.



where the fluidity decreased as the sphere size increased. In the medium cylinder the two opposing effects are so nearly balanced that the behaviour approximates that of a Newtonian fluid.

The evaluation of thixotropy may be performed more successfully. The method of Scott Blair (1935), mentioned above, was ".....timing the fall of a steel ball through a sample of honey which has been left to stand overnight, disintegrating the gel by stirring it with a perforated metal disk, and then timing a second ball of the same size." Pryce-Jones objects to this method because, after stirring, the sphere descends more rapidly and comparison is not made at the same shearing force. This brings the anomalous viscosity of the medium into the measurement. Such a difficulty can be eliminated by defining the magnitude of the thixotropy as the change in viscosity in poises, measured at zero shearing force, which occurs upon stirring. The determination of viscosity at zero shearing force may be accomplished as follows. A series of two or three spheres of the same density, but different radii is employed, observations with the smaller spheres being made first. Apparent viscosity is plotted against sphere radius and an extrapolation is made to zero sphere size, i. e., zero shearing force. The number of observations is restricted as much as possible to guard against stirring. In future work it may be found advantageous to extrapolate from the apparent viscosity-shearing force curve.

It is necessary to standardize the time of standing and the diameter of the container. In the following research, the time has been set at 48 hours and the diameter of the cylinder at 4.4 centimeters.

A number of honeys were examined for the presence and extent of thixotropy. It was found that over small shearing force intervals, in the standard container, apparent viscosity plotted against sphere radius gave a straight line. Therefore, in order to reduce the number of observations and eliminate stirring, in most cases measurements were made with two of the smaller spheres and two of the larger; these are represented by crosses in Figures XII to XVII. A line was drawn through these points and the extrapolation to zero sphere size made. Further observations were made, represented by squares in the figures. Data obtained after stirring are represented by circles. The stirring effect of the spheres is evident from these curves and the necessity for restricting the number of determinations employed in fixing the initial line becomes apparent.

The calculation of the thixotropy may be illustrated by Holly '31 honey, Figure XV. The unstirred honey was found, by extrapolation to have a viscosity of 274 poises at zero sphere size and zero shearing force. After stirring, this value changed to 260 poises. By the above definition the thixotropy is  $274 - 260$  or 14 poises.

Figures XII to XVII demonstrate the presence of anomalous viscosity. The viscosity of a true fluid such as invert sugar solution, Figure XVIII, is not influenced by the size of the sphere, while in each of the honeys shown, the apparent viscosity varies with this factor. The variations in anomalous viscosity were shown above to be erratic because of interfering factors; hence no rating of anomalous viscosity was made.

In Figure XII, the setting of the thixotropic gel is illustrated by the indicated increase in viscosity over a 48 hour period. The number of observations on Sweet Clover '33, Figure XIII, was great enough to cause appreciable stirring; but the difference in the value of the thixotropy due to this would not be over one poise. The invert sugar solution was observed before and after stirring and showed neither anomalous viscosity or thixotropy. The other curves are self-explanatory.

The values of thixotropy derived and other pertinent data are shown in Table 15.

There is no relationship visible between the nitrogen content, the calcium pectate number, or the volume of precipitate by the phosphotungstic acid method and the thixotropic ratings as summarized in Table 16. This does not mean, however, that protein is not associated with the thixotropy of honey, since pure sugar solutions have been shown to be non-thixotropic. Also, Pryce-Jones has demonstrated a general

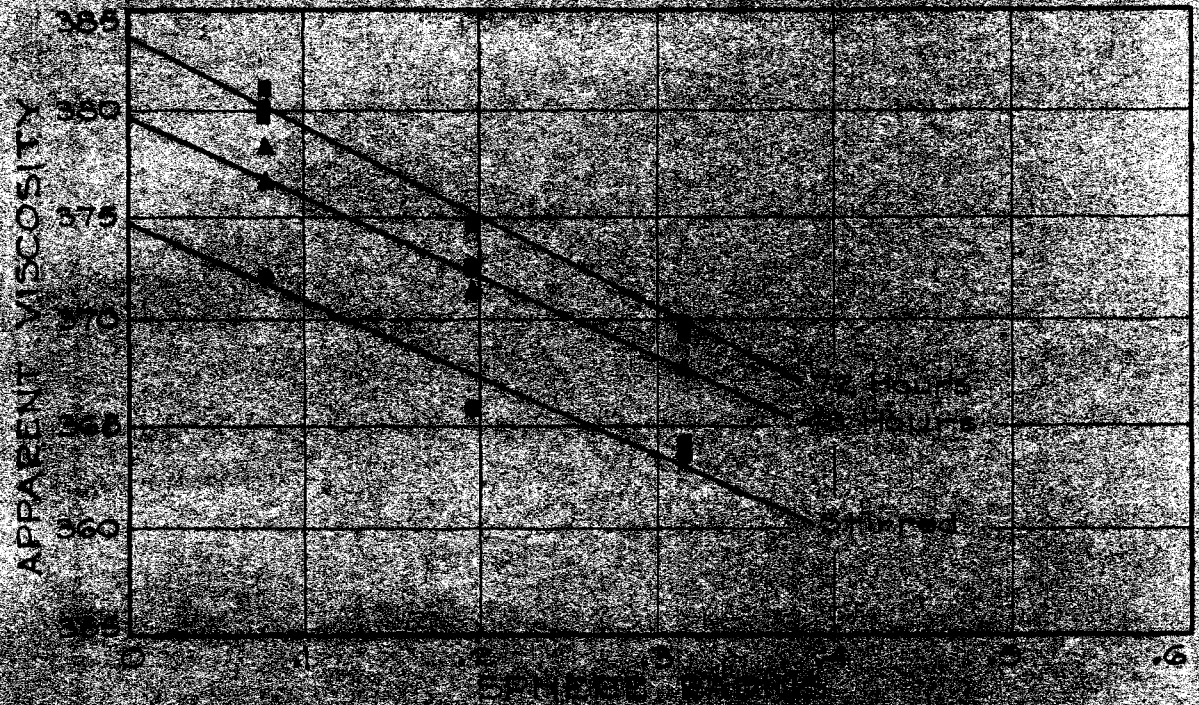


Figure 16. Apparent Viscosity of Sweet Clover Honey.

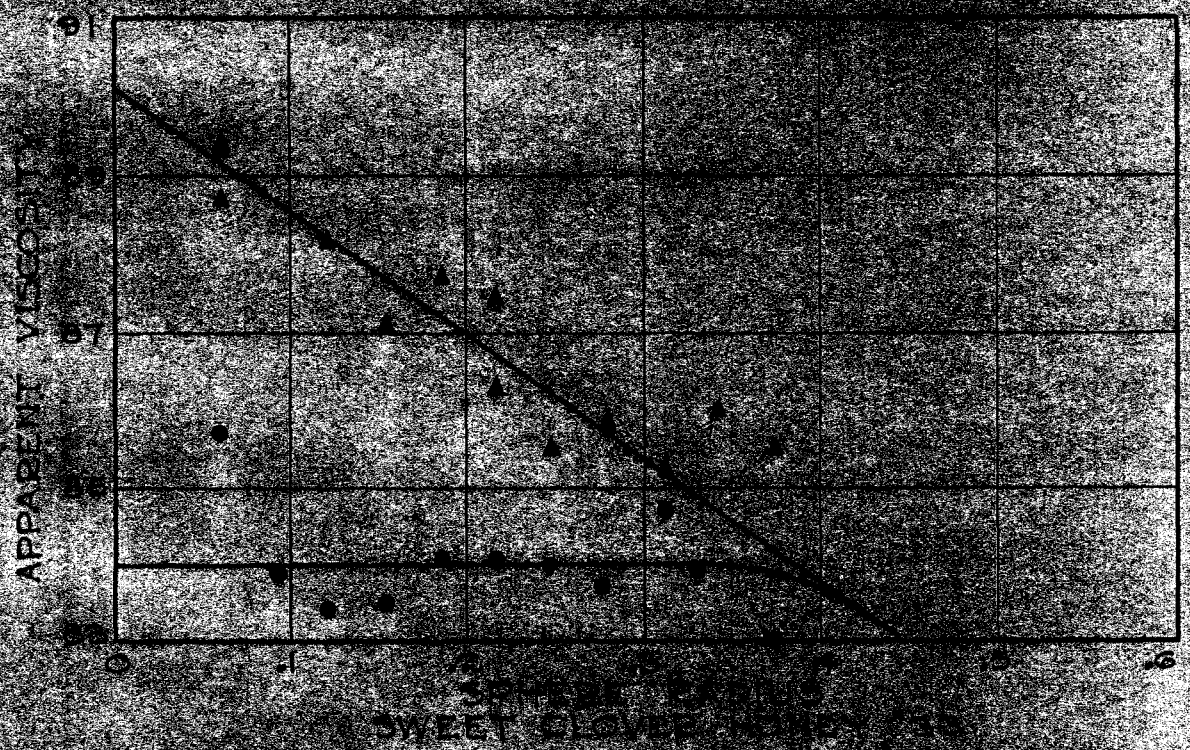


Figure 17. Apparent Viscosity of Sweet Clover Honey.



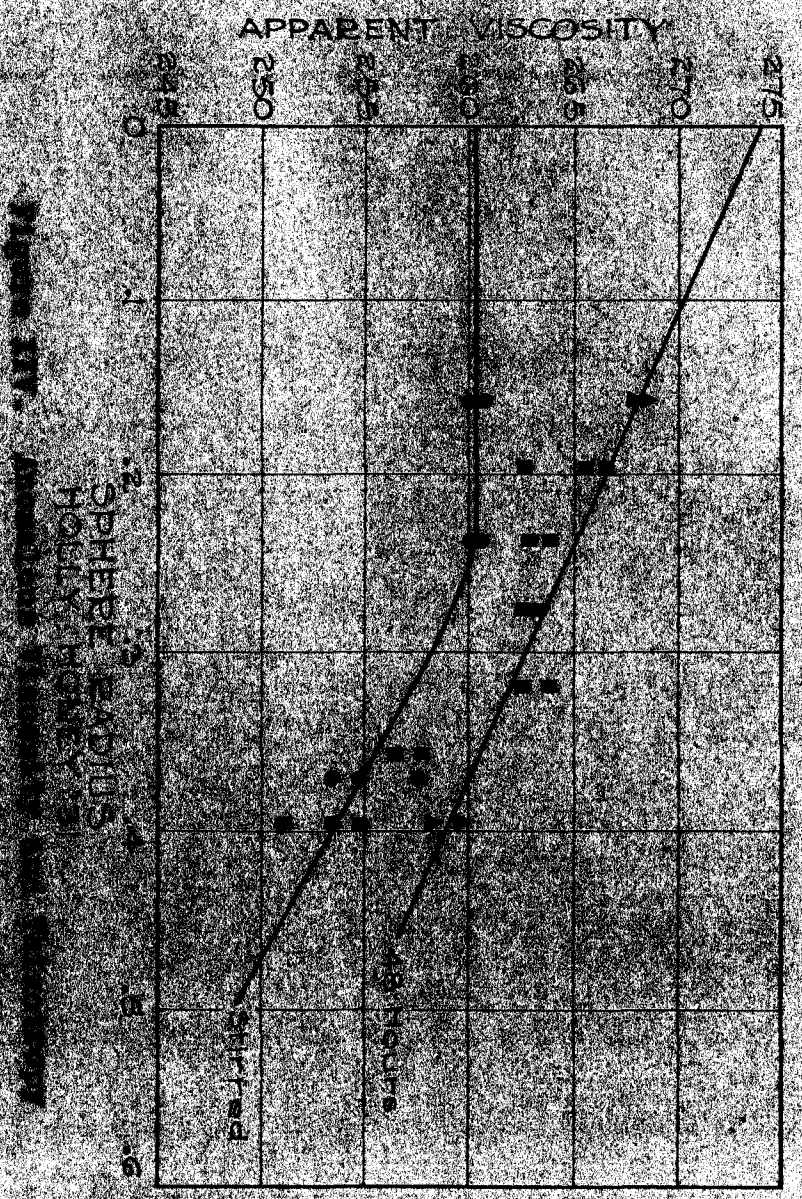
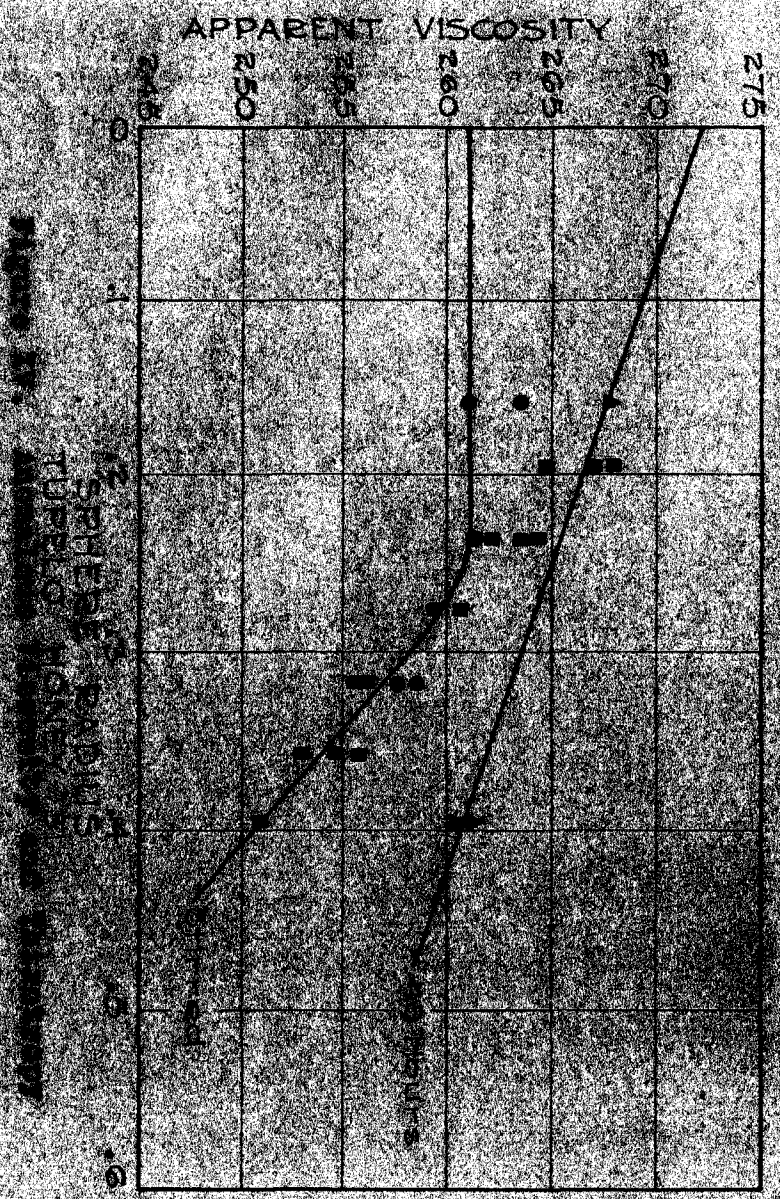
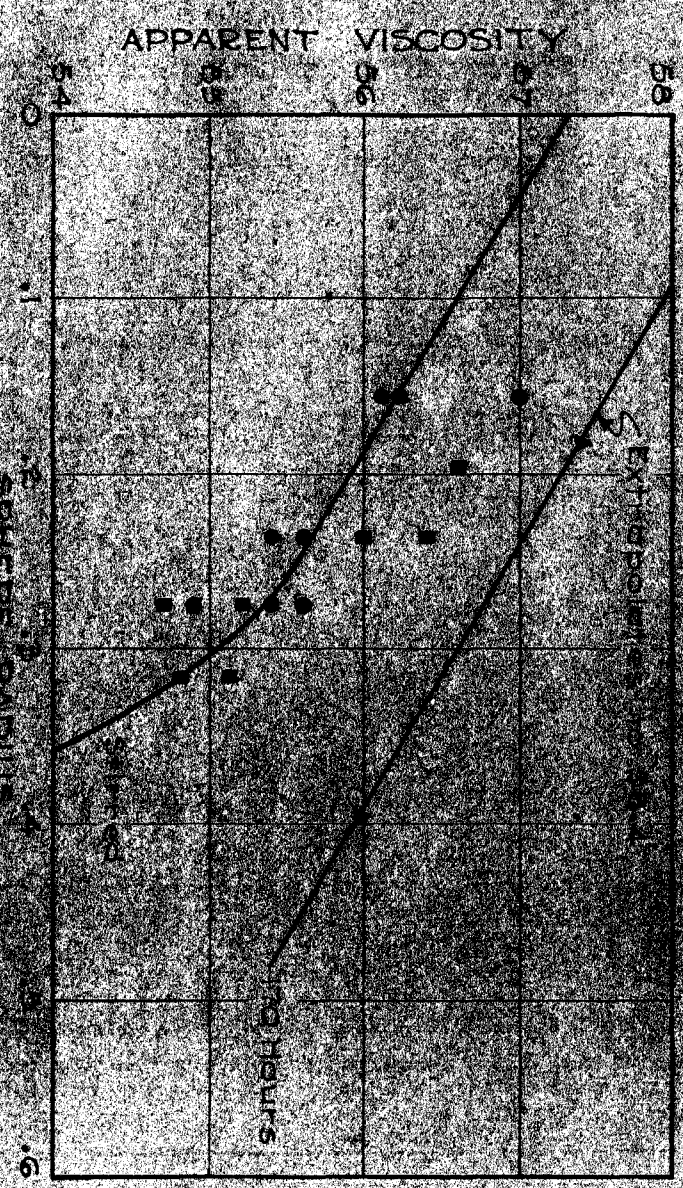


FIGURE VIII  
 SPHERE RADII  
 GAUFER, HONN, AND TILMANN



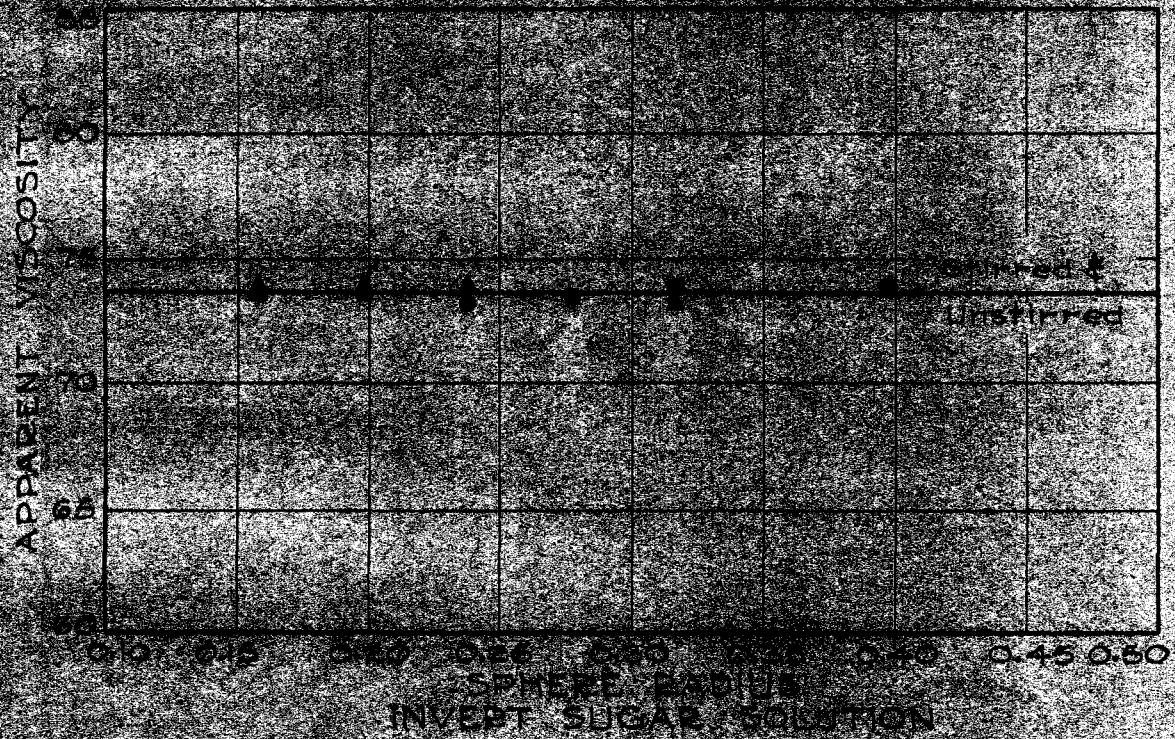


Figure VIII: Apparent Viscosity of an Invert Sugar Solution

Table 16

	Stood	N 24.7°	Thixotropy	Water %	Nitrogen %	Calcium pectate No.	Volume of Precipitate in cc.
Sweet Clover '36a	48 hrs.	379	5.0	15.0	0.032	0.016	0.3
Sweet Clover '36b	48 "	165		16.4			0.1
Sweet Clover '33	57 "	85	6.0	17.5	0.048	0.011	0.1
Holly '31	48 "	274	14.0	15.9	0.035	0.014	0.1
Tupelo '31	48 "	273	11.4	15.7	0.015	0.017	0.3
Sage '32	190 "	134	4.0	17.2	0.027	0.111	0.1
Galberry '32	170 "	58	2.5	19.1	0.049	0.108	0.1
Invert Sugar	48 "	74	0.0		0.000	0.000	0.0

correspondence between the volume of precipitate by the phosphotungstic acid method and the presence or "absence" of thixotropy. The data of this author cover a wide range of thixotropy, whereas the data of Table 16 are restricted to honeys which exhibit this condition only slightly. The honeys studied in the present research were so low in thixotropy and protein content that variation in the latter does not have a significant effect upon the former.

## V. SUMMARY AND CONCLUSIONS

Critical studies have been presented on the falling sphere viscometer as an instrument for obtaining information concerning certain properties of anomalous fluids. The equation of Prasynskii and Rabinovich, which makes possible the calculation of the velocity gradient and shearing force at the surface of the sphere, was found admirably adapted for use in the techniques developed.

The possibility of rating honeys on the basis of their deviation from true fluidity has been investigated, and it has been shown that there are opposing effects which, at the low rates of shear employed, tend to make such ratings erratic and difficult of interpretation. Thixotropy of the honeys was estimated by comparing viscosities of the sol (stirred) and gel (unstirred) forms of the honey, extrapolated to zero shear.

All of the honeys studied showed some degree of anomalous viscosity and thixotropy. These findings are at variance with the published statements of previous investigators who found the above phenomena only in heather honey. This disagreement lies in the fact that the very low thixotropy of non-heather honeys had not been detected by previous methods.

Other investigators found a general correlation between thixotropy and the colloidal content of the honey. The heather honey, for which thixotropy had been reported, con-

tained up to 6% of such materials. The colloidal content of the honeys studied in this thesis was less than 1% and the observed thixotropy was as low as one-one hundredth that of heather honey. It is not surprising, therefore, that no definite relationship was found between the colloidal content and thixotropy. However, an invert sugar solution did not show thixotropy. It may be inferred, therefore, that the low thixotropy of the honeys is associated with the colloidal material present.

VI. LITERATURE CITED

- Arnold, H. D. Limitations imposed by slip and inertia terms  
1911 upon Stokes' law for the motion of spheres through  
liquids. Phil. Mag. (6) 22, 755-775.
- Association of Official Agricultural Chemists, Official and  
tentative methods of analysis. 3rd Edition. Publish-  
ed by the association at Washington. 1930.
- Bacon, L. R. Measurement of absolute viscosity by the falling  
1936 sphere method. J. Franklin Inst. 221, 251-273.
- Barr, G. A monograph of viscometry. Oxford University Press.  
1931
- Bingham, E. C. Fluidity and plasticity. McGraw-Hill Book Co.,  
1922 New York. 1922.
- Bingham, E. C. Colloid types. Colloid Symposium Monograph 5,  
1928 219-238.
- Bogue, R. H. The sol-gel equilibrium in protein systems.  
1922 J. Am. Chem. Soc. 44, 1313-1322.
- Brindle, H. and Rowson, J. M. The apparent viscosity and  
1936 suspending power of mucilage of tragacanth and the  
evaluation of tragacanth gum. Quart. J. Pharm.  
Pharmacol. 9, 161-173.
- Buston, H. W. Allen's commercial organic analysis. 5th edi-  
1933 tion, Vol. 10, pp. 509-544. J. and A. Churchill,  
London. 1933.
- Carre', M. H. and Haynes, D. The estimation of pectin as  
1922 calcium pectate and the application of this method to  
the determination of the soluble pectin in apples.  
Biochem. J. 16, 60-69.
- Chataway, H. D. The determination of moisture in honey.  
1932 Can. J. Research 6, 532-547.
- Cheshire, F. R. Bees and beekeeping. Vol. 2, p. 487.  
1888 L. Upcott Gill, London. 1888.
- Coumou, J. Enkele waarnemingen over de structuur-viscositeit  
1935 van oplossingen van hoogpolymere stoffen. Chem.  
Weekblad. 32, 426-429.



- DeBoer, H. W. and Kniphorst, L. G. E. Thixotropie van  
1932 Heidehonig, Chem. Weekblad 29, 536-534.
- Derjaguine, B. and Wolarowitsch, M. Mesure de la viscosité  
1934 du verre fondu, et vérification de la formula de H.  
leChatelier. J. chim. phys. 31, 471-488.
- De Waele, A. The thixotropy of pseudoplastic systems.  
1931 J. Rheol. 2, 141-159.
- De Waele, A. and Dinnis, G. The double mobility of some  
1936 non-Newtonian fluids with particular reference to  
cellulose nitrate sols. Physics 7, 426-431.
- Eisenschitz, R. Über die Viskosimetrie von Kolloiden,  
1933 insbesondere der Lösungen von Zelluloseestern.  
Kolloid-Z. 64, 184-195.
- Faxen, H. Die Bewegung einer starren Kugel längs der Achse  
1922 eines mit zäher Flüssigkeit gefüllten Rohres.  
Arkiv Mat. Astron. Fysik 17, No. 27, 1-28.
- Fellenberg, T. Viskositätsbestimmungen in Honig. Mitt.  
1911 Lebensm. Hyg. 2, 161-178.
- Francis, A. W. Wall effect in falling ball method for  
1933 viscosity. Physics 4, 403-406.
- Freundlich, H. and Rawitzer, W. Über die Thixotropie des  
1927 konzentrierten Eisenoxydsols. Kolloidchem. Beihefte  
25, 231-278.
- Freundlich, H. Ueber thixotropie. Kolloid-Z. 46, 289-299.  
1928
- Fulmer E. I., Bosch, W., Park, O. W. and Buchanan, J. H.  
1934 The analysis of the water content of honey by use of  
the refractometer. Am. Bee J. 12, 208-212.
- Fulmer, E. I., Park, O. W. and Williams, J. C. The relation  
1935 between the rate of granulation of clover honey and  
its water content. Iowa State Apiarist Report 1935,  
62-63.
- Fulmer, E. I. and Williams, J. C. A method for the determina-  
1936 tion of the wall correction for the falling sphere  
viscometer. J. Phys. Chem. 40, 143-149.
- Gibson, W. H. and Jacobs, L. M. The falling sphere viscometer.  
1930 J. Chem. Soc. 117, 473-478.

- Glikman, S. A. Thixotropic viscosity of cellulose esters.  
1932 The theory and experimental data on anomalous viscosities of colloidal solutions. (Translated title) *Plasticheskie Massy* 1932, Nos. 2-4, 16-23.  
(Orig. not seen) *Chem. Abstr.* 27, 2615, (1933).
- Glikman, S. A. Thixotropic viscosity (Translated title)  
1935 *Zhur. Fiz. Khim. (Leningr.)* 6, 511-512.
- Hauser, E. A. Thixotropy as a contribution to structure  
1930 research of colloids. *Soc. Chem. Ind., Chem. Eng. Group, Proc.* 11-12, 137-141.
- Hauser, E. A. A contribution to the theory of thixotropy.  
1931 *J. Rheol.* 2, 5-9.
- Hauser, E. A. Über die Thixotropie von Dispersionen geringer  
1929 Konzentration. *Kolloid-Z.* 48, 57-62.
- Hirata, F. and Kube, K. Recherche sur le mesure de la  
1934 viscosité anormale par le moyen de la chute de bille.  
*J. Soc. Chem. Ind., Japan* 37, Supple. binding 11-14.
- Kulakoff, N. N. Über Viskosität und Plastizität disperser  
1937 Systeme, XI. Vergleich von drei Methoden zur Bestimmung der plastisch-viskosen Eigenschaften der Torfmasse. *Kolloid-Z.* 80, 204, 212.
- Ladenburg, R. Über den Einfluss von Wänden auf die Bewegung  
1907 einer Kugel in einer reibenden Flüssigkeit. *Ann. Physik* 23, 447-458.
- Lamb, H. *Hydrodynamics*. University Press, Cambridge. 1906  
1906
- Lemin, C. E. Motion of a sphere through a viscous liquid.  
1931 *Phil. Mag. (7)* 12, 589-596.
- McBain, J. W. and Watts, O. O. The structural properties of  
1932 anisotropic solutions of soap as determined by a new centrifugal falling ball method. *J. Rheol.* 3, 437-460.
- Paine, H. S., Gertler, S. I. and Lothrop, R. E. Colloidal  
1934 constituents of honey. *Ind. Eng. Chem.* 26, 73-81.
- Paine, H. S. and Lothrop, R. E. A small plant for filtering  
1935 honey. *Am. Bee J.* 75, 326-330.
- Parks, G. S., Barton, L. E., Spaght, M. E. and Richardson, J. W.  
1934 The viscosity of undercooled liquid glucose. *Physics* 5, 193-199.

- Pasynskii, A. G. and Rabinovich, A. I. The viscometry of  
1934 highly viscous lyophilic colloids. II Application  
of viscometers based on Stokes' law. (Translated  
title). Zhur. Fiz. Khim. (Leningr.) 5, 521-533.
- Phipps, H. E. The falling sphere viscometer and plasticity  
1928 measurements. Colloid Symposium Monograph 5, 259-266.
- Pryce-Jones, J. Thixotropy. J. Oil and Colour Chem. Assoc.  
1934 17, 305-375.
- Pryce-Jones, J. Some fundamental aspects of thixotropy.  
1936a J. Oil and Colour Chem. Assoc. 19, 295-337.
- Pryce-Jones, J. Thixotropy and elastic-recoil in heather  
1936b honey. Bee World 17, 89-94.
- Richardson, E. G. Velocity gradient methods in rheology.  
1935 Physics 6, 273-277.
- Risga, P. The viscosity of honey in relation to extraction.  
1937 Bee World 18, 45-47.
- Schischtschenko, (Shishchenko), R. J. and Baklanov, W. I.  
1933 Die Hydraulische Theorie lehmiger Lösungen und ihre  
praktischen Anwendungen. Arbeiten des Aserbaid-  
shanschen Naphtha-Forschungs-institutes (Azerbaid-  
zhanskii Neftianoi institut Trudy (Baku)). Original  
not seen. Cited by Kulakoff (1937), p. 208.
- Scott Blair, G. W. The thixotropy of heather honey. J. Phys.  
1935 Chem. 39, 213-219.
- Scott Blair, G. W. and Morland, D. A physical test for ling  
1936 honey. J. Ministry Agri. (Gt. Brit.) 43, No. 7.
- Sheppard, S. E. The measurement of the absolute viscosity  
1917 of very viscous media. Ind. Eng. Chem. 9, 523-527.
- Skrjabin, (Skriabin), A. K. Bericht über die Arbeiten zur  
1936 Untersuchung der Viskosität der Hydromasse, Arbeiten  
des Torfinstitutes, Moscow 17, 7. Original not seen.  
Cited by Kulakoff (1937), p. 205.
- Speicher, J. K. and Pfeiffer, G. H. The falling ball method  
1928 for the measurement of apparent viscosity of nitro-  
cellulose solutions. Colloid Symposium Monograph 5,  
267-272.

Szegvari, A. and Schalek, E. Ueber Eisenoxydgallerten.  
1923 Kolloid-Z. 32, 318-319. Die langsame Koagulation  
konzentrierter Eisenoxydsole zu reversiblen  
Gallerten. Zolloid-Z. 33, 326-334.

Thöni, J. Die Verwendung der quantitativen Präzipitin  
1911 reaktion bei Honiguntersuchungen. Mitt. Lebensm.  
Hyg. 2, 80-123.