

AN INVESTIGATION OF METHODS FOR THE DETERMINATION OF THE  
" COLLOIDAL PARTICLE SIZE OF VISCOSE

A THESIS

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By

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DEDICATION

This small contribution is dedicated to H. I. M.,  
C. H. M., and my wife, Mary Merwin Sweet, without whose most  
generous encouragement, self-sacrifice, and material assistance  
this work could not have been done.

Warren William Sweet.

## FOREWORD

The author wishes to acknowledge the direction and assistance of Dr. P. C. Scherer, Jr., who suggested this problem and under whom the work was done.

The author is most grateful for the hearty cooperation, encouragement, and assistance of the personnel of the Virginia Polytechnic Institute in the solution of the many problems which arose during the conduct of this investigation.

## I. INTRODUCTION

In 1893 Cross, Bevan, and Beadle announced the discovery of viscose and its use in the production of artificial filaments and membranes. Since that time great progress has been made in the development of the machinery and technique of production, without any appreciable change being made in the basic chemical operations underlying the process.

The chemistry of the process has received a great deal of attention from many workers (2, 3, 4, 5), but due to the complexity of the reactions many conflicting theories have been developed. The ageing or ripening of the viscose syrup is the most important step in the entire process and it is upon this step that the greater part of the work has been done. Any means of simplifying or shortening the ripening operation would release a large portion of the investment in the plant.

During the last few years the chemistry of the colloidal state has been developed into an exact science. Viscose as a colloid has received very little attention in the past, but from the success achieved in other fields from the study of colloidal conditions, colloid science should prove a useful tool in the study of viscose.

### Viscose as a colloid and the ripening process.

Gaebel (6) classifies viscose as a lyophile colloid. (7) is recommended for a thorough discussion of the terms and theories of colloid chemistry.

Herzog (8) considers the ripening of viscose to consist of the formation or building up of secondary particles from the free primary particles and the various phenomena observed in the process may be explained by the form and size of the secondary particles.

Berl and Lange (9) conclude from viscosity studies that ripening of viscose is not a polymerization effect, but is due to decomposition of the xanthate to xanthic acid and cellulose and the latter then coagulates.

Faust (10) mentions and discusses different theories of the colloidal structure of cellulose. He adds: to bring cellulose into solution it is first necessary to change the cell structure, as the compact natural cellulose is insoluble. The ripening of cellulose in alkali is accompanied by a shortening of the cell and a decrease in particle size, making it more easily reacted upon. The increased solubility of cellulose xanthate is due to a deep-seated deorientation and deformation of the previously well-oriented micelli. The increased hydration then gives the micelle a more spherical shape. Too marked a destruction of the bonds in the micelle detracts from the spinning quality of the artificial silk.

Mukoyama (11) measured the viscosity of viscose solutions of varying age. These all showed "structure viscosity" and the older solutions exhibited structure turbulence. The absolute value of the critical velocity corresponding with this structure turbulence decreases with increasing age of solution. Mukoyama (12) also studied syneresis of viscose gels, gel coagulation, viscosity minima of viscose solutions and their change with time and the surface tension

of viscose solutions.

Atsuki, Okamura and Matsuda (13) studied the reactions involved in ripening of viscose and the colloidal changes in viscose with changes in the concentration of sodium hydroxide.

Atsuki and Sobue (14) studied the structure of cellulose gels and the mechanism of gelation and syneresis.

Purpose of problem.

The purpose of this problem is to investigate the various methods which could possibly be used to accurately determine the particle size of the viscose sol, with the view of using the best method to follow the colloidal changes in ripening viscose.

## II. PREPARATION OF THE VISCOSE

The viscose for these experiments was prepared from Brown Company Alpha-Cellulose pulp, having the following analysis:

Total cellulose	99.43%
Alpha cellulose	93.15%
Moisture	5.77%
Ash	0.15%
Copper number	0.08
Viscosity	610 centipoises

The methods of analysis were those recommended by G. A. Richter (15).

The pulp was dipped in 18% NaOH solution for one hour at room temperature. The sheets were then removed to the hydraulic press and pressure applied until the press cake weighed 3.33 times the weight of the bone dry pulp. The press cake was then separated and ground in a water-cooled mixer and shredder for two hours. The crumbs thus produced were stored for ageing in a constant temperature room at 18° C for sixty to seventy hours.

The crumbs analyzed for different batches:

Fluff test	210-235
NaOH	12.9-14.3%
Stock	31.0-32.5%

The crumbs were then placed in an air-tight drum under a vacuum of about twenty-eight inches of mercury and CS<sub>2</sub> introduced in an amount calculated as 37% of the stock present in the crumbs. The xanthation was carried out at temperatures ranging from 25°-30° C, depending upon conditions in the laboratory. The drum and contents were revolved at about 5 r. p. m. for one hour and forty-five minutes

up to two hours, or until vacuum redeveloped in the drum. The xanthate crumbs were removed and placed in NaOH solution, so calculated that the final solution should contain 6.5% NaOH and 7.0% alpha cellulose. The mixture was placed in two-quart fruit jars and tumbled for two hours. The resulting syrup was filtered through cotton, centrifuged or placed away as is to age at 18° C.

### III. PARTICLE SIZE FROM BROWNIAN MOVEMENT.

Dr. P. C. Scherer had observed particles in Brownian motion in viscose in an improvised ultramicroscope and suggested the use of this phenomena to determine the size or molecular weight of the colloidal viscose particles.

#### Formula for Brownian Movement.

Burton (16) gives the following discussion of this method:

"Brownian movement is the name given to the continual zigzag motion possessed by small particles held in suspension in liquids or gases; it has been shown to be due to collisions between the particles and the molecules of the medium. The connection between the extent of the motion, the time of observation, and other factors has been worked out theoretically in various ways by Einstein, Smoluchowski, and Langevin." (See Svedberg (17) and Taylor (18) ).

As a result of this work we have the formula:

$$D^2 = \frac{R}{N} \times \frac{Tt}{3\pi\eta} \times \frac{1}{a}$$

Where:

D represents the displacement in centimeters parallel to any direction in t Seconds of a spherical particle of radius a, due to collisions with the molecules of the liquid medium, where R and N are the ordinary gas constants (numerically equal respectively to  $83 \times 10^6$  and  $7 \times 10^{23}$ ), T the absolute temperature and  $\eta$  the viscosity of the medium. It is important to notice the relation between D and t; on account of the random, zigzag nature of the motion, the displacement is

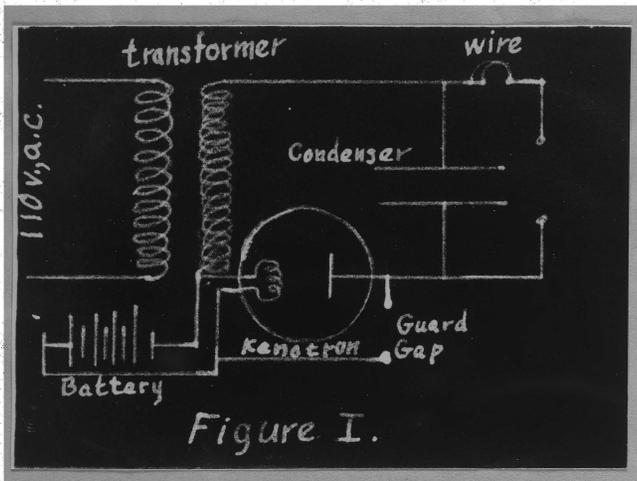


Figure I.

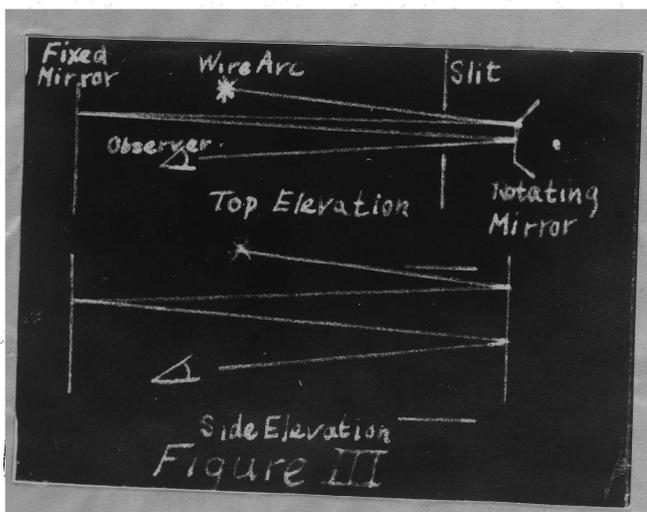
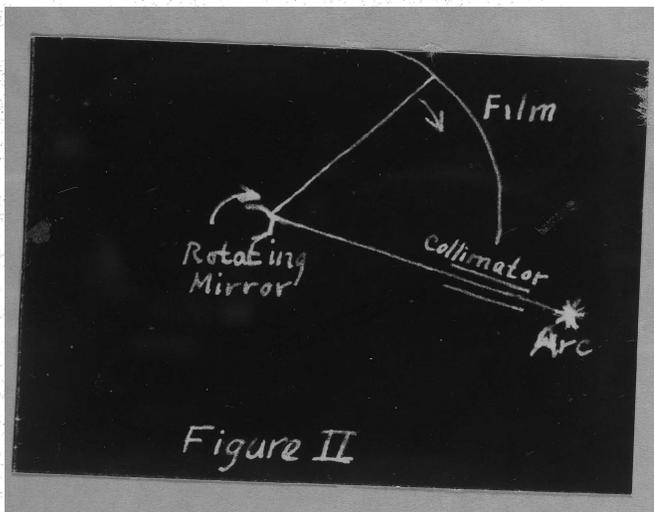
proportional to the square root of  $t$  and not to  $t$  simply. In other words a calculated value of the velocity  $D/t$  is not constant, but depends upon the value of  $t$  itself.

Method for illumination of particle.

Of course, the smaller  $t$  becomes, the more likely is  $D/t$  to become constant. Therefore, it was decided to measure the displacement of the particles in the viscose by photographing them by means of a brilliant light of short but known duration. The light was to be obtained by the method of J. A. Anderson (19), (20), Wendt and Irion (21), Anderson and Smith (22), and Nagaoka and Futogami (23).

The method of Anderson and his followers consists of impressing a high potential current upon a fine metallic wire in series with a spark gap, a condenser of high capacity being placed across the high potential supply to the wire and gap. The entire circuit is shown in figure I. When the potential has been built up to the proper point, the current breaks across the gap and a heavy surge of current passes through the wire, vaporizing it, giving a flash approaching  $10^{-6}$  seconds in duration, depending upon the characteristics of the circuit and the size of the wire.

The duration of the flash was to be measured by reflecting the light from the face of a rapidly rotating mirror driven by an air turbine or fixed on a J. W. Beam's top. The light would fall upon a portion of sensitized film fixed in an arc of constant radius to the axis of rotation of the mirror. The flash of light would leave a trace upon the film, and knowing the rate of rotation of the mirror,



the distance from the mirror to the film and the length of the trace, the duration of the flash could be calculated. See figure II.

Another method proposed (but not attempted) for the illumination of the particle was the electromagnetic shutter of J. W. Beams (25). This would undoubtedly be the most accurate and satisfactory method, provided all the necessary apparatus could be obtained.

#### Rate of rotation of mirror.

The rate of rotation of the mirror would be required for the calculation. Two methods were proposed for the determination of this.

The first method consisted of passing the light from a constant source through the upper part of a long, vertical slit onto the mirror, which would reflect it back through the slit while a face was normal to the incident ray. This ray would then fall upon a stationary mirror and be returned to the rotating mirror, and, if the face of the latter had not turned too far during the period for it to go out and back, the ray would finally be passed out through the slit and into the eye piece. According to Michelson (26), if we know the width of the slit and the distance from the slit to the stationary mirror when the latter is drawn away until the light in the eyepiece is just extinguished, and the velocity of light, we can calculate very accurately the rate of rotation of the mirror. See figure III.

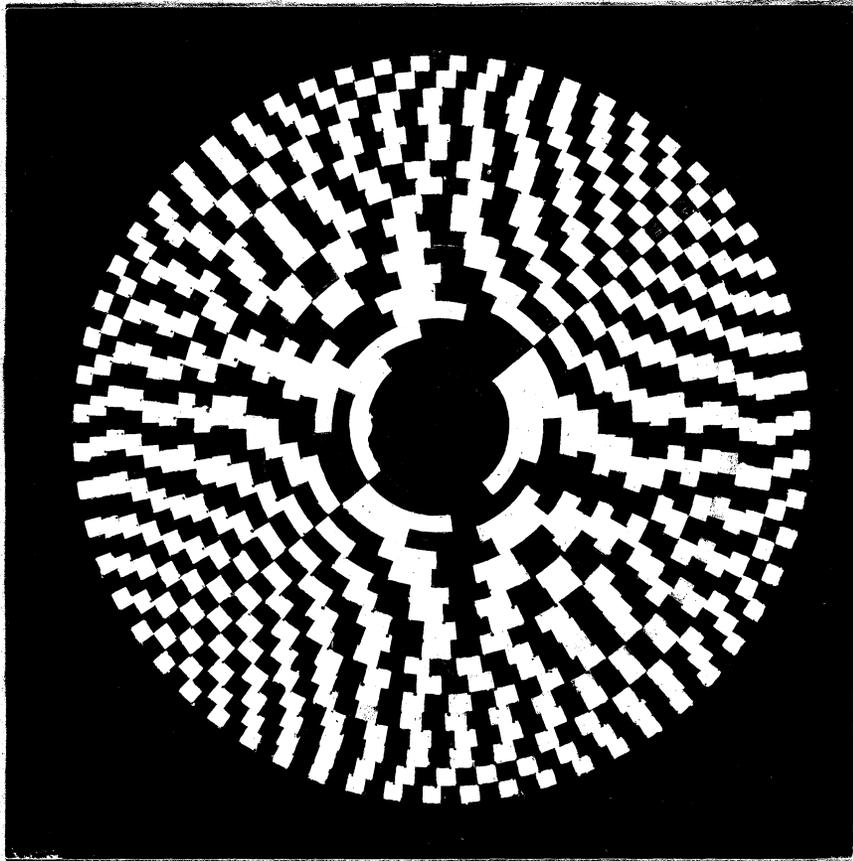


Figure IV.

The second method involves the use of a stroboscope disc (27, 28), see figure IV. The disc consists of concentric circles of prime numbers of white segments, the central circles containing the smallest number. The disc is rotated by a constant speed electric motor and arranged so that it can be seen once in every revolution of the rotating body under examination. The product of the circle or circles appearing to stand still and the rate of rotation of the disc gives the rate of rotation of the observed body.

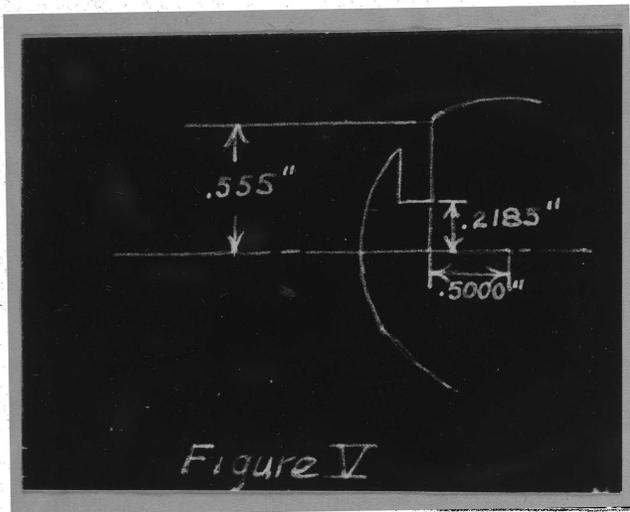
#### Observation of the particles.

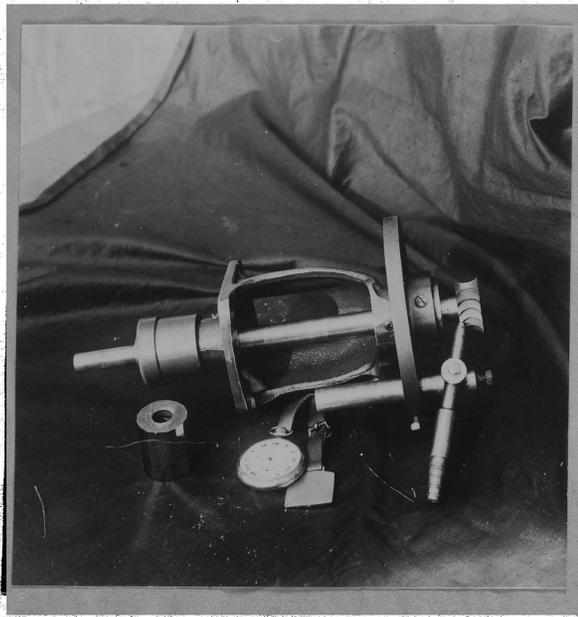
The particles are observed and photographed by means of an ultramicroscope fitted with a camera. The sol is placed in a specially prepared quartz cell and illuminated by means of a dark field cardioid condenser.

#### Application.

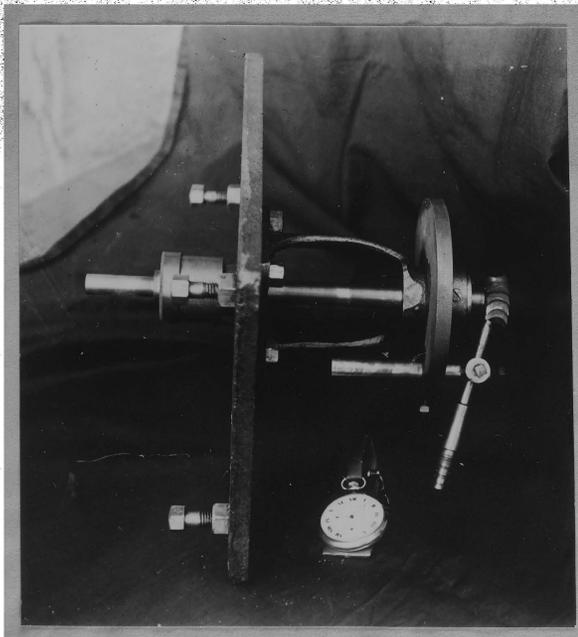
Some viscose, full strength, and dilutions of one-half, one-tenth and one-twentieth, made with 6.5% NaOH, previously aged to an ammonium chloride number of 15 were examined in the ultramicroscope by means of the 4 m. m. objective, giving a magnification of approximately 450 diameters. All but the full strength viscose showed particles in Brownian motion. When the oil immersion lens was tried, it was found that its N. A. value was too high, so a funnel stop was ordered to reduce this value. While waiting for the funnel stop, the turbine and electrical apparatus were constructed.

The turbine was constructed in the college shops. The





**Figure VI.**



**Figure VII.**



Figure IX

frame is that of a Ford Model A radiator pump. The shaft is 5/8" cold rolled steel shafting running in two SKF magneto bearings, jam fitted into each end of the frame and onto the shaft. The turbine wheel is the Terry reaction type cut on a milling machine from a chrome nickel steel disc 9/16" thick by 1 1/2" O. S. diameter. The buckets were cut with an end mill, 5/8" diameter by 1/8". See figure V. The reaction wheel is jam fitted onto the shaft. The nozzle is of the expansion type and is held in a universal clamp which permits its being set at any angle in relation to the wheel. The mirror, of sixteen faces, was machined from 1 1/2" manganese steel stock on a dividing head miller and each face relieved two thousandths of an inch on a magnetic chuck grinder. It was bored to give a tight slip fit onto the turbine shaft. The whole assembly is shown in figures VI, VII, and VIII.

The mirror was thoroughly cleaned and copper-plated in a cyanide bath. The plate was polished on the instrument shown in figure IX. This was arranged to draw the mirror back and forth over succeeding fine grades of emery paper, polishing each face in succession. The mirror was then nickel-plated and polished with tripoli and fine alumina.

The turbine was set in a frame of six by six timbers and surrounded by pieces of stone bench topping. The nozzle was connected up to the laboratory air supply. The air was turned onto the turbine gently for several days until well worn in, when high pressure was turned into it. It vibrated terrifically until the levelling screws were set on blocks of rubber. This stopped all of the audible

vibration except for a little at the critical speed.

Determination of the rate of rotation by means of the slit method was attempted, but it was found that the parallel light beam required was not bright enough and proper lining up of slit and mirrors was not possible with the equipment at hand. The surface of the mirror had not turned out to be as satisfactory a reflecting surface as had been hoped for at first.

The stroboscope wheel was then constructed. It was made of Upson Board, painted a dull black with lampblack and shellac. The circles were laid out and divided by means of the dividing head of a milling machine and the spots painted in by hand with white enamel. The disc was mounted on an induction motor, with a potentiometer hookup to the 110 a. c. line and a voltmeter across the motor terminals to keep the voltage constant.

The lower half of the rotating mirror was painted black, except for one face, which was left clear. The light from a d. c. carbon arc was concentrated on the lower half of the mirror and the stroboscope so placed that when the light fell on the clear face of the mirror, the stroboscope received the light reflected from it. With the entire apparatus enclosed in a dark room, this meant that the disc could be seen once in every revolution *of* the mirror.

With thirty pounds per square inch of air pressure being applied to the nozzle, the turbine was found by this method to be doing 91,425 r. p. m. The disc rotating at 1725 r. p. m. and the row with 53 sectors seemed to be standing still, so that  $1725 \times 53$  gives 91,425 r. p. m. While operating at this speed the mirror was

examined through a telescopic cathetometer and found to pass through periodic vibrations with an amplitude approaching 0.3 m. m. This would cause serious error in the wire flash as a trace on sensitized film.

The apparatus for burning out the wires was also constructed. The high potential transformer was regulated by means of taps from an auto transformer acting as a step-down transformer. This was done because the high potential transformer gave 142,000 volts with 220 volts on the primary, while 90,000 volts were all that the apparatus available could care for.

The condenser was constructed of window glass plates, 3 to 4 m. m. thick and wood pulp sheets boiled in paraffin separating coke tin plates 11 m. m. apart. There was a glass plate on each side of each tin plate and the rest of the space was occupied by the paraffin impregnated pulp sheets. The condenser was put together while the pulp sheets were fresh from the hot paraffin bath. When completely assembled it was weighted down with about three hundred pounds of iron and lead scrap and stored at 60°C for several hours to expel all air and excess paraffin from the inside of the condenser.

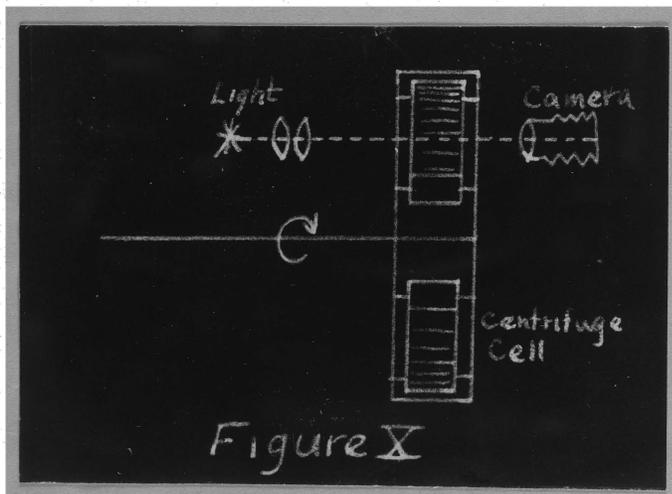
The assembled apparatus operates in this fashion. The rectified current from the KenotYon tube passes into the condenser where it is stored up until a sufficient potential is developed to break across the gap in series with the wire, which will then cause the wire to burn out. The gap between the terminals of the KenotYon is set to break down at 100,000 volts in order to protect the tube.

The entire electrical apparatus was assembled and tested and

several fine cooper wires burned out in an apparently very short time interval. The condenser was then placed on its side in a large open wooden box and paraffin cast underneath it and around the four edges, leaving the top open. When tested, it stood up as before. Several weeks later the condenser broke down during operation, apparently due to moisture abosrbed from the atmosphere through the paraffin.

The funnel stop for the oil immersion lens was now at hand and the ultramicroscope was set up as before, using the a. c. carbon arc for a light source. Viscose solutions of the same conditions as the previous ones were examined with the oil immersion lens, giving a magnification of 950 diameters. With this magnification it could be seen that the particles in motion consisted of various sized particles of dirt and residues of undissovled cellulose cells. These were all suspended in a field glowing with a very faint, bluish Tyndall light. Most of the grit and dirt could be removed by repeated filtering through cotton or centrifuging, but the residual fiber fragments were particularly persistent. No truly colloidal amierons were visible, which would be expected in a lyophile sol.

These conditions were found by R. Bernhardt (29), who investigated viscose microscopically with a view to its filtering qualities. He found microscopically visible particles of inorganic impurities from the pulp and caustic, iron from the equipment, particles of incompletely reacted cellulose from the mercerizing and xanthating operations, droplets of  $CS_2$  and air bubbles. The particles of unreacted cellulose were particularly persistent, even after repeated filtrations.



#### IV. PARTICLE SIZE BY THE ULTRACENTRIFUGE.

##### Ultracentrifuge.

Svedberg and his associates (30-35) have developed and refined the ultracentrifuge and the technique of its application until it promises to be the most accurate method for the determination of particle size in highly dispersed sols. J. B. Nichols (36) gives the following concise discussion of this method.

##### Principles Involved.

The principle of the ultracentrifuge is illustrated in Figure X. A transparent cell containing the solution or suspension to be studied is rotated at a speed sufficient to produce a centrifugal force 1000 to 100,000 times that of gravity. A beam of light passes up through the cell and permits the colorimetric determination, either by visual examination or by photographic recording, of the changes undergone by the solution while the centrifuge is in action. If the solution contains equal-sized particles and the centrifuging is rapid enough, a sharp boundary moves outward. The particle size can then be determined by measuring the displacement of the boundary  $x_2 - x_1$  in the time interval  $t_2 - t_1$ , and applying a modified form of Stoke's law. With nonuniform material, however, a partial separation is effected, giving one an opportunity to determine the distribution of sizes present from an analysis of the radial variation in concentration (37).

From the molecular-kinetic standpoint there is no distinction between a colloidal particle and a molecule in solution (38). The kinetic energy of any suspended unit which retains its identity is the

same as that of a molecule; therefore, the term "micellar weight" will be used as a generic name for the weight of either a suspended particle or a molecule in solution. "Particle size" will be used to designate the equivalent radius of the molecule or particle. Depending upon the experimental conditions, micellar weight or particle size may be determined either by the establishment of a sedimentation equilibrium between centrifuging and diffusion or by the measurement of the sedimentation velocity and of the diffusion (39).

### Theory.

At sedimentation equilibrium the change in free energy,  $dF$ , or the change in concentration with time,  $dc/dt$ , becomes equal to zero at every point in the cell; integration of the basic differential equations give the following relations for micellar weight (40):

$$M = \frac{2RT \ln \frac{c_2}{c_1}}{(1 - V\rho) \omega^2 (x_2^2 - x_1^2)} \quad (1)$$

For particle size the relation is

$$r = \sqrt[3]{\frac{3RT \ln \frac{c_2}{c_1}}{2N\pi(\rho_p - \rho_m)\omega^2(x_2^2 - x_1^2)}} \quad (1a)$$

where  $M$  is the micellar weight,  $r$  the effective radius of the particle considered as a sphere,  $R$  the gas constant,  $83.2 \times 10^6$ ,  $T$  the absolute temperature,  $N$  the Avogadro number,  $V$  the partial specific volume of the substance,  $\rho$  the density of the solution,  $\rho_p$  the density of the particle,  $\rho_m$  the density of the solvent,  $\omega$  the angular velocity, and  $c_2$  and  $c_1$  the concentrations at the points  $x_2$  and  $x_1$  distant from the

the axis of rotation of the centrifuge. The concentration is determined by the light-absorption method or in terms of the refractive index by Lamm's method (6). No assumptions have been made in Equation 1 as to form and structure of the molecule or particle. In addition, there are no membrane complications as in the osmotic-pressure method of determining micellar weight, and the presence of electrolytes is beneficial rather than harmful in that electrical potentials due to the separation of electrical charges having different mobilities are repressed.

On the assumption that the frictional force per mole is the same for sedimentation and for diffusion, the following simple sedimentation-velocity equations for small x-intervals are obtained:

$$M = \frac{RTs}{(1 - v\rho)D} \quad (2)$$

or

$$r = \sqrt{\frac{9\eta s}{2(\rho - \rho_m)}} \quad (2a)$$

Both  $D$ , the diffusion constant, and  $s$ , the sedimentation constant ( $1/\omega^2 x \cdot dx/dt$ ), characteristic of each molecular species or particle size, are calculated directly from the data obtained during the centrifuging (41).

#### Requirements for satisfactory operation.

A centrifuge developing a centrifugal force of 1000 to 10,000 times that of gravity renders possible the study of the sedimentation velocities of the lyophobic inorganic colloids and the sedimentation equilibria of the proteins and other organic lyophilic

substances of micellar weight greater than 10,000. For the determination of the sedimentation velocities of these lyophilic substances and for the sedimentation equilibria of most substances in the range 10,000 to 1000, centrifugal forces of about 100,000 times that of gravity are required.

The most important conditions for satisfactory ultracentrifugal analysis are: First, no vibrational or thermal effects should disturb the sedimenting system; second, the amplitude of vibrations of the rotor must be small enough and the optical system well enough defined that sharp pictures can be obtained; third, cells should be constructed to withstand the pressures of 100 to 200 atmospheres produced when the centrifugal force reaches the magnitude of 100,000 times that of gravity; and fourth, the substance must undergo no deterioration during the centrifuging.

## APPLICATION OF ULTRACENTRIFUGE

This method was surveyed with the purpose in view of applying it to this problem, using the air turbine as the rotor. But the latter vibrated too much to consider using it, and in addition the necessary auxiliary optical equipment was not available. It was estimated that the machine work and equipment to set up this apparatus would cost at least one thousand five hundred dollars.

A. J. Stamm (35) made just one determination on viscose with his ultracentrifuge during his studies of the degree of dispersion of cellulose in cuprammonium solution. This was made on a 0.26% viscose solution in 2.2% sodium hydroxide. The viscose was prepared from cotton linters alpha cellulose. The relative viscosity of the solution was 2.17. The diffusion and sedimentation values were of the same order of magnitude as those for cellulose in cuprammonium solvent. He, therefore, concludes that the molecular weight of cellulose xanthogenate in the viscose solution must then be very similar to molecular weight found for cellulose in cuprammonium solvent,  $40,000 \pm 5000$ . He had difficulties in all his work with cellulose in obtaining concordant results at concentrations much above 0.2% of cellulose, due to molecular attraction and entangling of the probably rod-shaped micelli.

## V. PARTICLE SIZE BY THE MICRO-INTERFEROMETER

U. Gerhardt (42, 43, 44) has developed an accurate method for the determination of particle diameter in lyophobic sols, applying Michelson's method for the measurement of double stars to the particle image in the ultramicroscope. The particle is illuminated on opposite ends of the same diameter by covering up all but a small portion of opposite ends of a diameter of the annular opening in the Cardioid condenser. A diaphragm carrying two pin holes is mounted between the objective and eyepiece of the microscope. The mechanism of the diaphragm sets the pin holes at any desired separation along a line passing through the optical axis of the microscope at a right angle.

The images of the particles appear banded when viewed with the instrument set up as above. The graduated knob on the diaphragm is turned until the bands on the particular particle under observation disappear and it appears as a single spot of light. Then, as the diaphragm knob is calibrated in separation of the pin holes, the particle diameter can be calculated from the following formula:

$$d = \frac{\lambda}{4S} \sqrt{4l^2 + S^2}$$

Where  $d$  is the particle diameter,  $\lambda$  is the wave length of the light used,  $l$  is the distance in centimeters of the pin holes from the particle and  $S$ , the separation in centimeters of the pin holes.

In Gerhardt's instrument  $l$  was fixed and  $S$  variable.

In the instrument used here  $S$  was fixed and  $l$  was variable.

#### Application.

As the condioid condenser was out of adjustment, it had been returned to the factory for servicing. A dark field condenser was improvised from an Abbe substage illuminator by inserting, in the ground glass holder underneath, circles of opaque black photographic paper with notches cut on the opposite ends of a diameter of the disc. The proper size of the notch was found by experiment. This turned out to be a very satisfactory dark field illuminator.

The mechanism for separating the pin holes was beyond the reach of the funds of this laboratory. So the distance between them was fixed by punching them in a thin piece of aluminum foil cemented to the bottom of the microscope draw tube. After several trials a pair properly centered were obtained. The distance to the particle was varied by working the draw tube of the microscope in and out.

The bands in the particle image could not be made to blend. The particle merely went out of focus as the draw tube was moved in and out.

After the observation was made concerning the condition of the sol, this method was abandoned as useless, the particles in question not giving a visible image.

## VI. PARTICLE SIZE BY CATAPHORESIS

Until very recently the cataphoresis or electrolytic migration of the colloid substance has been a phenomenon thoroughly relied upon by authoritative colloid investigators for the indication of particle size.

Svedberg and Anderson (45) have discussed and criticized the various experimental methods for the measurement of electrolytic cataphoresis. Kruyt (46) and Tuorila (47) have brought the methods up to date.

Abrahamson and Michaelis state: "The electrophoretic mobility of microscopically visible particles is independent of size, shape and conductivity of the particles within the limits of the experimental errors of the apparatus. This is valid for extreme variations in size, shape and conductivity."

Kruyt (49) gives the following formulae for calculating the particle size of lyophile colloids:

$$(1) \frac{\eta_s - \eta_0}{\eta_0} = \frac{5}{2} \phi \left[ 1 + \frac{1}{\kappa \eta r^2} \left( \frac{\rho D^2}{2\pi} \right) \right]$$

Where  $\eta_s$  and  $\eta_0$  are the absolute viscosities of the sol for two different concentrations of an added electrolyte,  $\eta$  the viscosity of the unchanged sol,  $\kappa$  the specific conductance,  $r$  the radius of the particle,  $D$  the dielectric constant and  $\rho$  the electrokinetic potential of the electric double layer.  $\kappa$  and  $D$  are determined in the standard conductivity apparatus.  $\phi$  is the volume

of the dispersed particles.

$\mathcal{J}$  is found from:

$$\mathcal{J} = \frac{6\pi\eta}{HD} \cdot U$$

Where H is the potential gradient in volts per centimeter and U the cataphoretic velocity of the colloid under the electrical pressure of H.

These various factors are obtained by introducing the sol under some of the pure solvent in a U tube free of constrictions and applying a direct current through the entire system by means of electrodes just dipping under the surface of the liquid in each arm of the tube. U is found from the rate at which the boundary between sol and solvent moves up or down the tube under the applied potential. H is found dividing the potential difference between the two electrodes by the mean distance through the sol and solvent which separates them. This leaves  $\phi$  and  $\mathcal{V}$  the only factor which cannot be determined by experiment. These two are determined by getting two values for the left of (1) and solving simultaneously.

Kruyt makes the following criticism: "In the above calculation it was assumed, however, that  $\mathcal{J}$  varies on the addition of an electrolyte, but that  $\phi$  and  $\mathcal{V}$  do not. Unfortunately, we cannot, a priori, predict that this will be so.

#### Application.

This method was tried to see how viscose would behave under the electric current. Freshly prepared viscose was introduced under

6.5% NaOH solution in a U tube containing electrodes connected through a rheostat to the laboratory 110 v. d. c. supply. A voltmeter was connected across the electrodes. The boundary was observed by throwing the light from a 200-watt Mazda lamp through a slit into the tube at right angles to the line of sight.

No mention of the boundary could be observed until a potential of 80 volts was reached. This caused the solutions to heat to the point where the viscose coagulated very rapidly. The viscose drew up into a point when the boundary did move.

The colored matter moved up into the arm containing the positive pole and after one of the U tubes had stood a few weeks a faint flocculent skeleton appeared in the arm containing the negative pole. This appeared to be cellulose which would indicate that it had been attracted to the negatively charged electrode.

The NaOH required to keep the viscose fluid seems to be too good a conductor to permit the far less mobile cellulose or xanthate particles to be affected by the current. The heating effect even in a water bath is too great to permit the current to be left on any length of time without materially affecting the viscose.

## VII. TYNDALL EFFECT IN THE DETERMINATION OF PARTICLE SIZE.

The phenomenon of the scattering of light by colloidal solutions is called the Tyndall Effect. It is, generally speaking, caused by particles smaller than the wave length of the light, which scatter the light, thereby polarizing it at the same time. It is produced by illuminating the sol with a beam of intense light, producing an illuminated path through the liquid. Albert Einstein (50) has given a thorough mathematical development of the theoretical relationships underlying the phenomenon. Krishnamurti (51) has developed the theory in relation to the theories of gelation. The scattered light is generally polarized to a greater or lesser extent, but no mathematical relationships have been developed for this condition.

Rayleigh (52, 53, 54) has developed several empirical formulas for the calculation of particle size from the intensity of the scattered light. These apply only to lyophobic or suspensoid sols.

The work that has been done on lyophilic sols has resulted in purely empirical data and has not been tied up with any of the established methods for the estimation of particle size.

Mie (55) has studied the absorption and scattering of light by colloidal solutions containing particles of various dimensions and has concluded that at constant concentration the intensity of the scattered light increases with the size of the particles and is proportional to their volume.

Burton and Annetts (56), applied Martin and Swertzer's (57)

method for the study of coagulation phenomena in gels.

Mardles (58) made quantitative measurements of the "tyndall number" of coagulating cellulose acetate gels and found the light dispersed to be at a maximum at the point of coagulation.

Prasad, Mehta and Desai (59) studied the scattered light from gel, forming silicic acid mixtures by means of a Nutting photometer in conjunction with a Hilger wave-length spectrometer, and concluded that the particles in a gel are larger than in the sol.

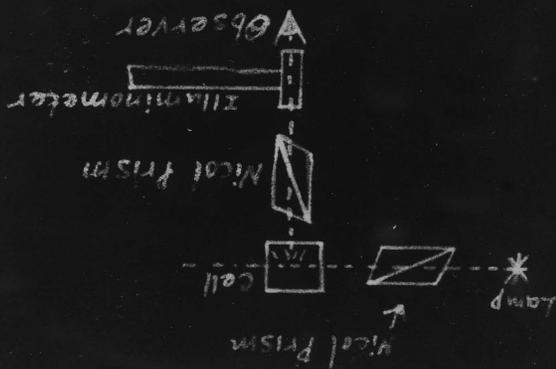
Andreev (60) has developed an instrument containing a very sensitive photoelectric cell for the study of scattered light which will remove the factor of human error in the observations. No results have been announced.

Herzog and Lange (61) worked on a method for characterizing colloidal solutions by the state of polarization of their tyndall light. They found that with a constant wave length of illumination and constant refractive index of the particle that the angle of polarization of the Tyndall light is proportional to the particle size. With cellulose acetate dissolved in methyl acetate, the polarization angle decreased with increasing age of solution. They claimed this indicated progressive decrease in particle size. The changes were more marked in dilute solutions, best results below 0.08% cellulose acetate, while considerable difficulty was found in making measurements on solutions containing as low as 2.5% cellulose acetate.

#### Application.

A study of the intensity of the Tyndall light of viscose solutions of different concentrations of cellulose was made as the

Figure XI



solutions aged. A diagram of the apparatus is shown in figure XI. The light source was a 60-watt 110-volt Mazda lamp supplied through a rheostat and having a voltmeter across the terminals of the lamp. The voltage was maintained at 105 volts while observations were being made. The intensity of the Tyndall light was measured by means of a Leeds and Northrup illuminometer. No consistent changes in the intensity of the beam could be detected as the solutions aged.

The solutions were all observed in the same cell, the light beam always entering at the same point and the observations being made always at the same place in the cell.

The polarization of the Tyndall light of viscose as the solutions aged was studied in an apparatus similar to that just given, except that a fixed Nicol prism was placed between the light source and the cell and a rotatable Nicol prism placed between the illuminometer and cell. Intensity readings were taken at the positions of maximum and minimum transmission of the second Nicol. At the position of minimum transmission the light was so weak as to introduce a very serious error in the form of eye-fatigue.

The change of color of the viscose from yellow through red to brown introduced a serious error also.

No concordant results could be obtained by this method, although from purely visual observation, it appeared that the difference between the minimum and maximum intensities decreased with ageing of the solutions.

In order to overcome the effect of changing hue, strips of photographic film, cleared in hypo and stained with weak solutions of Easter egg dyes to match the color of the solution, were placed in front of the

illuminometer. But these could not be tinted with sufficient accuracy to be of any value.

In order to overcome both the eye fatigue and color errors, a Weston phototronic cell was put in the place of the illuminometer. But even the light at maximum transmission was too weak to cause the most delicate galvanometer available to show a deflection when connected to the phototronic cell.

It is believed that a very sensitive radiation thermopile or bolometer, together with a bright source of monochromatic illumination might yield some valuable results by this method.

### VIII. PARTICLE SIZE BY X-RAYS

A very thorough review and discussion of the application of x-rays to the study of colloids has been given by G. L. Clark (62).

By virtue of the fact that the diffraction lines from crystalline particles with a diameter less than  $10^{-6}$  cm. become broader, Debye and Scherrer (62) were able to derive their equation connecting line breadth with particle size:

$$B = 2 \sqrt{\frac{\log_e R}{\pi}} \cdot \frac{\lambda}{D (\cos \frac{\theta}{2})} + b$$

Where B is the angular breadth of a diffraction halo measured between points of half maximum intensity,  $\theta$  is the diffraction angle,  $\lambda$  the wave-length, D the average thickness of the crystal parallel to a cubic axis and b the minimum breadth determined by the particular apparatus.

#### Application.

This method was tried on viscose syrup. The viscose was placed between two microscope cover glasses and these were then fastened to the under side of a 3/8 inch lead plate, covering the 1/64 inch pin-hole drilled in the plate. A panchromatic plate in a holder with a paper cover was placed 12 centimeters below the sample. The dental x-ray tube of the Physics Department was placed about two feet away from the plate and aimed so the rays would pass

straight down through the pin-hole onto the plate. Exposures totalling ten minutes in duration were made of the sample. Upon development of the plate all that appeared was a pin-hole photograph of the target. This was repeated several times with the same results.

The difficulty probably lay in the fact that the tube gave off "white" x-rays (tungsten target) instead of monochromatic and the pin hole was not long enough to prevent the lens effect and its consequent photographing of the target.

## IX. PARTICLE SIZE BY THE ERIOMETER

Young (63) measured the particle size of films of milk and other emulsions by means of his eriometer. This consists of a large opaque sheet or plate with a hole 0.5 m. m. in diameter in the middle, surrounded by a concentric circle of small holes. The source of parallel light is placed behind the plate and the sol between two sheets of glass in front of it, parallel to the perforated sheet and located so that the light from the central hole falls on the middle of the sol holder. A diffraction ring should now appear around the central spot of light. The sol is drawn away from the plate until the diffraction ring coincides with the other circle. The distance of the suspension from the perforated plate is proportional to the particle diameter. The apparatus must be calibrated against sols containing particles of known size.

This method was tried on several viscose solutions with a piece of opaque card perforated as specified. No diffraction ring was observed, even when the parallel rays from the condensing system of the carbon arc were used.

## X. TRANSMITTED LIGHT AND VISCOSE

To complete the list of possible methods for the determination of ageing phenomena in viscose, several empirical methods involving the effect of the viscose on transmitted light were studied.

### Refractive Index.

Refractive index readings on viscose from the time of solution to setting to a gel gave 1.373 continuously. Herzog (64) found 1.375.

### Turbidity.

No measurements were made of changes in turbidity of viscose while ageing, due to lack of equipment for the purpose.

Mukoyama (65) found that the turbidity of a freshly prepared sol increases linearly with concentration, but after a few days the increase of turbidity with concentration becomes much greater, reaches a maximum and then falls off, the departure from the original sol increasing with the age.

### An-isotropy.

Faust (66) found that viscose solution showed no streaming double refraction or other double refraction effects.

The author observed viscose flowing through narrow tubes, in the line of flow and at right angles to it, through a nicol prism. No an-isotropic effect could be observed.

Viscose was found to be too turbid to observe through a standard polarimeter.

The fibers which remain undissolved in viscose show up very

brilliantly against a black field when viewed through the polarizing microscope with the Nicol prisms set for minimum transmission.

#### Spierrer Lens.

Seifrizz (67) describes a new type of oil immersion microscope objective in which the dark field effect is incorporated. This was accomplished by sputtering the under side of the next to the bottom lens in the objective through a pin hole shield inside a cathode ray tube, so that a very small opaque disc is placed in the optical center of the lens. The size of the disc is arranged so as to cut off all the direct rays entering from the object, but passing to the upper lens system, the oblique rays. This is claimed to bring out microscopic objects which ordinarily are not shown by visible light, due to their index of refraction being very nearly the same as their suspending medium.

A lens similar to this was approximated in this laboratory from a Bausch and Lomb oil immersion objective having separable lenses, by placing tiny drops of black pyroxylin lacquer between the two bottom lenses until <sup>a</sup> disc of the proper size and very nearly centered was obtained.

When used with the Cornu condenser or the Abbe substage illuminator this lens showed up the undissolved fiber fragments and dirt very plainly, but did not bring out the colloidal particles.

## XI. CONCLUSIONS

1. Viscose contains varying amounts of dirt and undissolved fiber fragments which cannot be completely removed by filtration and which appear to be colloidal particles in Brownian motion under low magnifications.

2. These particles should be completely removed, probably by means of a super-centrifuge, before any serious study of the optical phenomena of viscose is undertaken.

3. The lyophile colloidal particles in viscose could not be delineated by any of the available methods.

4. None of the methods which were tried can be used directly for the determination of the particle size of viscose.

5. From the success achieved with the ultracentrifuge on other lyophile colloids, this would appear to be the best method for the direct determination of the size of the size of the colloidal particle in viscose.

## B I B L I O G R A P H Y

- (1) Cross, Bevan & Beadle, Ber. 26, 1090 (1893)
- (2) Gaebel, "Technologie der Textilfasern", H. O. Herzog, Ed., VII Band, pp. 135-46. Springer, Berlin, 1927.
- (3) Heuser, West & Esselen, "Textbook of Cellulose Chemistry", pp 62-75. McGraw-Hill, 1924.
- (4) Schorger, "The Chemistry of Cellulose and Wood", pp 254-61. McGraw-Hill, 1926.
- (5) Giern. Chim. Ind. Applicata., 13, 476-9 (1931), Vitale.
- (6) Gaebel, "Technologie der Textilfasern", q. v., pp 139.
- (7) Kruyt & van Klooster, "Colloids", Wiley, 1927.
- (8) Herzog, Pulp & Paper Mag. of Canada, 24, 699-703(1926)
- (9) Berl & Lange, Cellulose Chemie, 7, 145-7.
- (10) Faust, Kolloid-Z. 46, 329-36(1928)
- (11) Mukoyama, Ibid., 41, 62-71 (1927)

- (12) Mukoyama, Ibid., 42, 79-86(1927).
- (13) Atsuki, Okamura & Matsuda, J. Faculty Eng. Imp. Univ. Tokyo, 17, 135-51(1927).
- (14) Atsuki & Sobue, Proc. Imp. Acad. (Japan), 6, 161-4(1930).
- (15) Richter, Ind. Eng. Chem., 23, 131-39.
- (16) Burton, "Colloid Chemistry" (J. Alexander), pp172-173. Chemical Catalog, 1926.
- (17) Svedberg, "Colloid Chemistry", Chemical Catalog, 1924.
- (18) Taylor, "A Treatise on Physical Chemistry", pp 1572-1580. Van Nostrand, 1931.
- (19) Anderson, Proc. Nat. Acad. Sci., 6, 42-3(1920).
- (20) Anderson, Ibid., 8, 231-2(1922)
- (21) Wendt & Iriou, J. Am. Chem. Sec., 44, 1887-94(1922)
- (22) Anderson & Smith, Astrophys J. 64, 295-314(1926)
- (23) Nagaoka & Futogami, Inst. of Physical and Chem. Research, #150, Vol. 8, pp 261-288.
- (24) Beams, Rev. Sci. Instruments, 1, 667-71(1930)
- (25) Beams, J. Optical Sec. Am., 13, 597-601(1926)

- (27) Glazebrook, "Dictionary of Applied Physics",  
Vol. III. pp542-545, Macmillan, London, 1923.
- (28) Henriot & Huguenard, Génie Civil, 86, 538-9(1925)
- (29) Bernhardt, Kunstseide, 11, 13-7, 56, 85-90(1919)
- (30) Svedberg, "Colloid Chemistry", (q. v.) 2nd Ed.  
pp 146-167, Chemical Catalog, 1928.
- (31) Svedberg & Nichols, J. AM. Chem. Sec. 45, 2910.
- (32) Svedberg & Rinde, Ibid., 46, 2677.
- (33) Svedberg & Nichols, Ibid., 49, 2920.
- (34) Svedberg & Chinnoaga, Ibid., 50, 1407.
- (35) Stamm, Ibid., 52, 3047-62(1930).
- (36) Nichols, Ind. Eng. Chem. 4, 12-17(1932). Anal. Ed.
- (37) See (32).
- (38) Einstein, Ann. Physik., (40), 17, 549(1905)
- (39) Svedberg, Kolloid-Z. 36, 57(1925)
- (40) Svedberg & Nichols, J Am. Chem. Sec., 43, 3081(1926)
- (41) See (33)
- (42) Gerhardt, Z. Physik, 35, 697-718(1926)
- (43) Gerhardt, Ibid., 44, 397-402(1927)
- (44) Gerhardt, Ann. Physik, 87, 130-44(1928)
- (45) Svedberg & Anderson, Kolloid-Z. 24, 156-65(1919)

- (46) Kruyt & v. d. Willigen, Ibid., 44, 22-32(1928)
- (47) Tuorila, Ibid., 44, 11-22(1928)
- (48) Abramson & Michaelis, J. Gen. Physiol., 12, 587-97(1929)
- (49) Kruyt & Van Klooster, "Colloids", pp 173-175, Wiley, 1927.
- (50) Einstein, ref. (16), Chap. 15.
- (51) Krishnamurti, Proc. Royal Soc. (Lond.) A122, 76-103(1929).
- (52) Rayleigh, Phil. Mag. 107, 274 and 447(1871).
- (53) Rayleigh, Ibid., 12, 81(1881).
- (54) Rayleigh, Ibid., 47, 375(1899).
- (55) Mie, Proc. Roy. Soc. 122A, 76(1929).
- (56) Burton & Annetts, J. Phys. Chem. 35, 48-59(1931)
- (57) Martin, see ref. (16), p340.
- (58) Mardles, Trans. Faraday Soc. preprint 1922.
- (59) Prasad, Mehta & Desai, J. Phys. Chem., 36, 1324-1336(1932).
- (60) Andreev, Kolloid-Z. 57, 39-49(1931).
- (61) Herzog & Lange, Ber. 62B, 491-5(1929).

- (62) Clark, "Colloid Symposium Monograph", Vol. IV,  
pp145-73. Chemical Catalog, 1926.
- (63) Young, Phil. Mag. 20, 354(1885).
- (64) Gaebel, see p140, ref. (2).
- (65) Mukoyama, Kolloid-Z., 41, 158-63(1927)
- (66) Faust, Ber. 59B, 2912 - 20(1926)
- (67) Seifriz, J. Phys. Chem., 35, 118-129.