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entitled A Study of the Application of
Scientific Methods to the Testing of
Lithographic Ink.

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

Robert F. Reed,

Wayland M. Burgess, Chairman

A STUDY OF THE APPLICATION
OF
SCIENTIFIC METHODS
TO THE
TESTING OF LITHOGRAPHIC INKS

A thesis submitted to the
Graduate School
of the University of Cincinnati
in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1932
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Carl Joseph Opp

B. A. Miami University 1928
M. A. University of Cincinnati 1930

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DEFINITION AND CONCEPTION OF THE TERM INK

The word ink in its widest significance is a substance employed for producing a graphic tracing, inscription, or impression on paper or similar material. The term includes two distinct conditions of pigment or coloring matter: the one fluid, and prepared for use with pen or brush as a writing ink; the other is a glutinous, plastic, adhesive mass--printing ink, used in transferring impressions to paper (1).

(1) Encyclopedia Britannica, 14, 11th edition, p. 571

There are in general three kinds of printing, and it follows there are three kinds of printing inks. In the first method we have printing from raised surfaces commonly called letterpress printing; in the second method we have printing from a depressed surface, commonly called intaglio printing; and in the third we have the flat surface method or as it is better known, lithographic printing. There are many kinds of ink in each of these main divisions, manufactured with a view to their use on some special printing device.

The work in this thesis is concerned with the study of the inks of the lithographic type. This ink differs from the other two in that it is more concentrated, that

is, less fluid. It also has the ability to work in the presence of water, which is not necessarily true of the others.

History of Inks

Chinese records give us the name of the inventor of the writing brush (Mung T'ien about 200 B.C.), and rag paper (Ts'ai Lun in 105 A.D.). There is no name on record for the inventor of ink. The reason is that ink is not the invention of any one individual. The situation is much the same as that with regard to porcelain. It is not an invention that can be attributed to anyone in particular, but was a slow gradual process, and the outcome of the united exertions of men during several centuries. The same observation is true in the case of ink.

It is only natural to think that printing inks should date back to the first printing press. This would mean going back to about 1450, when John Gutenberg (2)

(2) Frank Wiborg, "History of Printing Ink", p. 88

started work on his first book. This book is now called the Gutenberg Bible, and, according to authentic history, is the first book to be printed by movable type.

In giving Gutenberg credit for the first printing ink, we forget about the Chinese. Certain things we consider to be quite modern, are to them very old stories. It seems quite certain that as early as 50 B.C. (3)

(3) Philip Ruxton, "Printing Inks" (1918), p. 7

a rather primitive method of printing was known to them. It can readily be seen that advances in the art of printing were necessarily difficult. In the Chinese language each word requires a separate character. Thus a job printer would require about 15,000 characters to meet only the very ordinary demands of his work.

However, as early as 927 A.D. certain volumes were printed from stone blocks for the Imperial college at Peking. In the printing of these books, the characters were cut into the stone so that when printed they appeared white on a black background. Shortly after, blocks of wood were used, on which the characters were raised, and the printed page appeared with black characters on a white background. It seems for ink they had a form of lamp black obtained from certain pine trees. It was merely necessary to mix this pigment with oil and gum to get a fairly satisfactory printing ink.

In Europe, printing as an art became quite general during the latter part of the 15th and early part of the 16th century. Many specimens of this early printing

exist in the various museums and are of great interest. In most cases the ink has remained an intense black with no signs of fading. This is no more than would be expected, for the pigment in these inks is chiefly carbon, one of the most stable and fastest pigments known.

The early printer usually made his own ink. This, of course, being before the time of division of labor. They usually used a heat-bodied linseed oil in their inks which served as the vehicle. The use of this substance necessitated the boiling of the oil and getting it to the proper thickness. This was a dangerous task, and frequently resulted in a fire.

It was therefore customary for the early printer and his staff to take a holiday in the fields when the ink supply got low. They would set up their kettles and proceed to boil the linseed oil. They thus combined the work of bodying the oil with pleasure. The day was usually ended with a picnic. The mixing of the pigment with the varnish thus prepared was then carried out at the printing shop and the other ingredients added to give the finished ink.

The scheme whereby the printer made his own ink was not satisfactory. In the first place it was a long tedious job, requiring a lot of time, and in the second place it often did not turn^{out} very well. Therefore, by the 17th century it was quite common for the printer to buy his inks ready made. This was not so good, because the printer was then at the mercy of the ink maker. This was

brought out by Moxon in his "Mechanik Exercises", (1683), in which he says, "instead of having good inks the printers content themselves by paying an ink-maker for a good ink, which may be better or worse according to the conscience of the ink maker".

There was considerable difference between the materials used by the early English and Dutch ink makers. The latter used only boiled linseed oil with a small amount of rosin, whereas the English added a considerable quantity of rosin, and even mineral oil to an insufficiently boiled linseed oil. Consequently, the English ink was an inferior product to that of the Dutch.

The art of printing from stone in the lithographic manner was discovered by Alois Senefelder, of Munich, Bavaria, in 1793. It was several years later before his invention was perfected. It is true in this case that the history of lithographic inks date back to the work of Senefelder, and his first press.

In 1817 he wrote and published an excellent book entitled "The Invention of Lithography", which is still considered a classic. In his book he gives a number of formulas for various types of lithographic inks. It is interesting to note that Senefelder's inks contained essentially the same ingredients as the lithographic inks of today. This shows the degree to which he had developed the process.

The latter part of the 18th century developed the use of litharge in boiling linseed oil. It did not receive universal sanction and was soon abandoned. The principle objection was that varnish prepared with litharge clogged the type. The early part of the 19th century saw the introduction of soap to make the ink leave a clean, sharp impression on the paper. The soaps had the further advantage of thickening the ink without the varnish being bodied to so great an extent by boiling.

In 1823 William Savage, who had studied the manufacture of printing inks from the point of view of the practical printer, published a book on "The Preparation of Printing Inks" in which he discussed the various methods of manufacture. His recommendation of old linseed oil brought forward an idea which has since received considerable attention from ink makers, namely, that an oil used for printing inks should be carefully purified. The old linseed oil would, of course, tend to be free from foots and sediment. However, if such an oil is not available, mechanical and chemical means must be employed to clarify it.

The 18th century developed the idea of adding a blue coloring matter to neutralize the yellow of the oil, in the preparation of black inks. Prussian blue and indigo are used for this purpose.

The 19th century saw the discovery and subsequent

introduction of pigments prepared from aniline dyes. This followed as a result of the synthesis by Perkin of mauve, the first aniline dye.

Meanwhile, owing to the desire to reduce the cost of inks and at the same time to secure inks which work better on the various grades of paper now being made, new oils began to be introduced into the ink vehicle. First of all came the introduction of rosin, and rosin oil, followed by mineral oil, the long gilsonites furnishing both pigment and vehicle. Since then the semi-drying oils such as corn oil and rape seed oil, and the new drying oils such as perilla, and China wood or Tung Oil have come into common use.

We thus arrive at the 20th century and find that there are 500-600 odd materials used for making inks. These materials have been studied principally from the practical point of view. However, the scientific investigation of inks has lagged behind the other developments. Just what physical and chemical effects a certain substance has upon an ink is in many cases not known.

Recent advances have been made along the line of mechanical devices for the manufacture of large quantities of ink at a minimum cost. The principle progress along the line of new materials has been in the preparation of colored pigments, used so effectively in multi-color work.

Introduction

A lithographic ink is a suspension of a pigment in a drying oil or varnish vehicle, together with bases and driers necessary to produce satisfactory working properties. Because of the individual differences in pigments and varnishes used, no definite statement will be made here concerning the proportions to be used in compounding a lithographic ink.

It has been suggested by a recent writer that when a statement is made in a book or article, that "it is difficult to state the proper constituents of printer's ink, you may be sure the author is a cautious man". (4)

(4) Andes, Louis, E., "Oil Colors and Printers' Inks" (1918), p. 205, Scott, Greenwood and Son, London.

Well it behooves the technical writer to be careful in making precise statements, and in this particular it would be difficult to give definite proportions of medium or varnish and dry color for manufacture of printing inks, for very good reasons. Take the varnish as an example. There is no absolute standard of viscosity for the different grades of varnish. The individual plant usually has a set of working standards, which are determined

empirically by the finger method. In the production of new batches, they match up the new sample with their standard. Consequently, as the standard changes with aging, oxidation, etc., the result is that inks which fail to work are quite frequently the outcome.

Grinding has an important influence upon the proportion of dry color, and the varnish required for printing inks. The work for which the printing ink is required, and the price at which it must be manufactured will all materially affect the proportionate quantities. Thus, where we are dealing with substances with so many variable properties, it is extremely difficult to state precisely the proportions and get duplicate results.

The characteristics of a lithographic ink include its ability to work satisfactorily in the presence of water. It is this property that distinguishes this type of ink from an ordinary printing ink.

It may be seen that lithographic inks are plastic materials composed of pigments dispersed in viscous, oily vehicles. In general the pigments are much the same as those used in the making of paints. The varnishes used as the dispersing medium are of one type, and that is the type which dries by oxidation. We thus have another characteristic difference between the lithographic ink and the printing ink, for example of the news ink type. In this ink, the vehicle is a non-oxidizing mineral oil. The

drying is accomplished by the vehicle being absorbed by the stock upon which it is printed.

Commercially, lithographic inks consist of 30 to 80% of pigment (depending upon the specific gravity and the oil absorption of the pigment), the remainder being varnish and small amounts of other materials such as soaps, waxes, driers, etc., which are added to modify their characteristics. Heat bodied linseed and perilla varnishes have been found to be the most satisfactory vehicles for inks of this nature. Perilla varnish is made from perilla oil in much the same way that linseed varnish is made by heating linseed oil. The oil is obtained from the perilla seed, (a small round seed, the scientific name of which is "perilla nankanensis"), a plant grown extensively in China and Japan (5).

(5) Gardner, H. A., "Paint Researches" (1917), p. 320

Lithographic inks, like many other present-day technical materials, have been evolved over a period of many years, starting long before the development of a science related to their chemical composition and structure.

It is an interesting as well as lamentable fact that in spite of the application of chemical and physical testing methods in the selection of raw materials, and the standardizing of finished products, that little progress

has been made in the application of science to the control of consistency of printing inks. At the beginning of this work there was little exact knowledge of the properties of the inks of this type. The facts known are largely empirical, that is, things learned through experience, which are often incapable of being expressed in scientific terms.

The physical properties of an ink can be described by the word consistency. This word is in itself meant to include three recognized properties, namely, mobility, length, and tack. These properties will be defined in terms of empirical tests which will now be described.

Mobility is the reciprocal of resistance to plastic flow. It is a term similar to that of fluidity as used in viscous flow. The mobility is usually measured by moving the finger about in a small globule of the ink on a glass plate or bond paper, observing the resistance to the movement of the finger. If the finger experiences little resistance in moving around in the smear of ink on the plate, it is said to have "high Mobility". However, if a considerable force is required to move the finger about in the ink, it is said to have "low Mobility".

Length may be defined as being the apparent coherence of the ink. At the present time it is measured by pulling a small quantity of ink from the glass plate with the middle finger and observing the length of the thread of ink produced.

Tack may be said to be "the resistance to separation or splitting of a small thin film of ink". It is usually measured by placing a small amount of ink on a glass plate, smearing it into a thin film, then pressing firmly with the finger, then lifting the finger quickly, noting the stickiness or resistance of the ink film.

When measuring the properties of inks in this manner, comparison with a standard ink is always made. As can be readily imagined, this method is not sufficiently accurate even for control.

Such testing methods as are described above, when carried out by an experienced ink man in conjunction with an actual printing trial on specified types of paper, provide a certain degree of standardization. However, it leaves something to be desired, especially since it is known that the consistencies of the "standard samples" and the samples being tested undergo a definite change with time.

Efforts have been made to apply the knowledge developed through research on other types of plastics to the control of the consistency of printing inks, but no satisfactory method has been developed, and little has been published on the subject. Basseches (6)

(6) Basseches, J. L., Journal Optical Society of America and Review of Scientific Instruments., 6, p. 875-895 (1922).

has drawn tentative conclusions regarding the nature of "length and tack" and proposed a rapid method of approximate measurement. Attempts have been made to apply the Bingham and Murray plastometer and the Gardner mobilometer. However, little progress has been made up to the present time in the scientific measurement of the physical properties of printing and lithographic inks.

The difficulties encountered in the measurement of materials of this nature in the standard plastometers are due partly to the high pressures required and to the low rates of flow produced. In the first place, to be of practical value as a control method, the test should not consume more than a few minutes. In the second place, the results should be capable of interpretation in terms of printing characteristics.

Object of the Research

The object of this research was to work out a method for the scientific measurement of the three factors, length, tack, and mobility. This, in turn, should lead to an interpretation of these vague terms in scientific language. This accomplishment should enable inks to be made according to scientific methods rather than by the cut and try process.

Thus, it is the aim of this research to place the testing of inks and ink materials on a scientific basis, and to remove, as much as possible, the human element in testing methods.

Experimental

Part I. Determination of the Physical and Chemical Properties of Materials Used.

In the preliminary work, the more important physical and chemical properties were determined. This was necessary in order to make it possible to duplicate results.

Linseed oil varnishes serve as the principal constituent of the vehicles of all lithographic inks. Their properties vary over a wide range, depending upon the methods of preparation. A complete line of linseed varnishes was obtained from the Ault and Wiborg Company. These ranged in consistency from raw linseed oil to number 7 varnish which has the lowest mobility.

Determination of Specific Gravity

The specific gravity of the various varnishes was determined by the pycnometer method. All determinations were made at 25 C. In the case of the heavier varnishes, the volume was obtained by difference. The pycnometer was partly filled with varnish, weighed, filled to the top with water and weighed again. From this data it was possible to calculate the weight per unit volume.

Determination of Absolute Viscosity

The practical importance of viscosity determinations

is admitted by all varnish technicians. Consequently some sort of a consistency test is applied in practically every plant where varnishes are made, but the methods are, as a rule, only qualitative. While it is possible for the experienced worker to estimate viscosity with a fair degree of accuracy in a comparative way, he usually has no means for expressing his observations in terms intelligible to others. For instance, in the case where some type of a commercial viscometer is used, relative viscosities thus determined are expressed in arbitrary units which are seldom comparable with results obtained with the same instruments of the same kind in different laboratories.

Consistency determinations of varnishes are made to insure uniform products. For this purpose it is a common practice to have a standard sample and compare with it each batch of material as manufactured. The objection to this method is the fact that the standards almost invariably change with time no matter how carefully they are made.

Relative viscosity methods prove fairly satisfactory for control work when accurate measurements are not necessary. In research work more precise measurements are required. In this work it was desirable to determine the viscosity in C.G.S. units. This unit is the "Poise" and is defined as that viscosity which a liquid possessed when a force of one dyne was necessary to cause two parallel

layers of liquid of unit area, and unit distance apart to slide past one another with unit velocity.

In selecting a viscometer for the given purpose, two points should be considered: (1) adaptability and (2) interpretation of results. No instrument yet devised is universally applicable in the industries and in purely scientific work. Viscometers which are suitable for one type of work and one kind of material may be entirely unsuitable for others.

There are in general three types of viscometers:

- (1) Efflux (capillary tube)
- (2) Torsion (rotating disk or cylinder)
- (3) Falling weight

It was found impractical to employ the capillary tube method in determining the viscosity of the whole range of varnishes. The method was applicable to the thin varnishes, but could not be used satisfactorily with the heavier semi-plastic ones.

No reliable instrument of the torsion type was available. Besides, an instrument of this type has to be calibrated against standard liquids before it can be used in determining absolute units of viscosity. The calibration involves nearly as much work as determining the viscosity of the varnish directly by some other method.

The method which was found to be applicable to practically the whole range was that of the falling ball. The time of the fall of a sphere in a liquid has been recognized

as an exact method since the work of Gibson and Jacobs (7)

(7) Gibson, W. H. and Jacobs, L. M., J. Chem. Soc., 117,
1920, p. 473

in which they added two corrections to Stoke's law:

$$v = \frac{2}{9} \frac{Gr^2}{n} \frac{d_s - d_l}{n}$$

where v = velocity of sphere

G = acceleration of gravity

r = radius of the sphere

d_s = density of the sphere

d_l = density of the liquid

n = viscosity of the liquid

For practical working purposes, two corrections must be introduced: (1) a correction for the confined space of the liquid, that is, the nearness of the walls of the vessel influences the velocity; and (2) the "end effect" of the bottom of the tube on velocity. The complete equation including these corrections for the fall of the sphere is given in the following equation as modified by Gibson and Jacobs (7).

$$n = \frac{2}{9} \frac{Gr^2 (d_s - d_l) T}{(1 + 2.4 x) (1 + 3.3 r/h) S}$$

where T = time taken for the sphere to fall through
distance S

x = ratio of the radius of the sphere to that of
the cylinder

h = height of the liquid

This equation gives, directly, a measure of absolute viscosity in poises when the C.G.S. units are employed.

A 250 c.c. graduate served as the cylinder in which the determinations were made. The inside diameter and height of the cylinder was accurately determined. Two marks, 15 centimeters apart, were etched around the cylinder so as to include the middle portion. The cylinder was then filled to the height of 27 cm. with the substance to be tested. This was placed in a constant temperature water bath maintained at 25.0 degrees C. and allowed to remain for twenty minutes. After coming to a constant temperature, the cylinder and contents were taken from the bath and a number of ball bearings of known and uniform diameter were allowed to fall through a glass tube into the liquid. The time of the fall of the sphere between the 15 cm. marks was determined by means of a stop-watch. In testing the less viscous varnishes, ball bearings 1/16 inch in diameter were used, and for the heavier ones the 5/32 inch balls were used.

The accuracy of this method was checked by determining the viscosity of castor oil by the efflux tube method. The precision of this latter method when carefully carried out with a capillary of known dimensions is considered unquestionable. The absolute viscosity of castor oil as determined by the falling ball method was 6.58 poises (average of six experiments). The viscosity as determined

by the flow through the capillary tube was found to be 6.61 poises (average of five determinations). This is a difference of 0.03 poises or 3 centipoises. These results indicate that the falling weight method checks the capillary tube method within less than 0.5 of one percent, to be exact, 0.456% difference.

Determination of Acid Value.

The acid value is a chemical property and may be defined as the number of milligrams of potassium hydroxide required to neutralize the free fatty acid in one gram of material. This value was determined by the method outlined and recommended by Larsen and Young (8)

(8) Larsen, L. M. and Young, W. J.,--Journal of Industrial and Engineering Chemistry, 17, 277 (1925).

In this method, neutral ether alone or a one to one mixture of ether and alcohol may be used. The ether by itself gives very gratifying results. The method is as follows: weigh out on an analytical balance 0.5 to 1.0 grams of material in a 100 c.c. erlenmeyer flask. Then add 50 c.c. of neutral ether. To hasten solution, the contents may be gently heated. After the solution of the varnish is obtained, 5 drops of phenolphthalein indicator are added. The titration is carried out with a 0.1 N alcoholic potassium hydroxide solution, the reacting mixture being

kept in constant motion by rotating the flask. Towards the end, the alkali is added drop by drop. The place at which the red coloration persists for 10 seconds or longer is taken as the end point.

Determination of Refractive Index.

Refractive indices of some of the samples of oils and varnishes used in this work were determined. These indices were determined by means of the Abbe refractometer. The refractive index is of value in detecting adulterants in oils and fats. Adulterants usually lower the refractive index, and this serves as a quick test.

The following table contains a summary of the results of the various tests made upon the materials used as ink vehicles in this study.

Table I

Physical and Chemical Properties of Linseed Oil and
Lithographic Varnishes.

Ault & Wiborg's Series	Sp. Gr. at 25 C. cf. H ₂ O	Absolute Vis. in poises at 25 C.	Acid Value (mg.KOH/gm)	N _D
Raw Linseed Oil	0.9413	1.24	4.28	1.4808
Boiled Oil	0.9478	1.75	6.23	1.4852
Number 0000	0.9551	4.94	10.58	1.4863
" 000	0.9591	9.70		
" 00	0.9624	14.12		1.4887
" 0	0.9634	17.50		
" 1	0.9709	60.62	15.60	1.4908
" 2	0.9735	115.6		
" 3	0.9745	206.3		
" 4	0.9765	603.0		
" 5	0.9778	1072.4		
" 6	0.9789	2160.5		
" 7	0.9782	1440.5	26.95	1.4933

Hydrous Aluminum Oxide

Due to the fact that little was known about the scientific measurement of the physical properties of lithographic inks, the samples prepared for study were of simple composition. It was considered advisable to limit the number of variables as far as possible so that the effects of the constituents could be isolated.

For the most part, therefore, the inks prepared in this study consisted of dispersions of hydrous aluminum oxide in varnishes of varying viscosity. Inks of different consistencies were thus prepared by varying the proportions of the pigment and vehicle.

The aluminum hydrate used was obtained from the International Printing Ink Corporation. This substance is itself a colloidal material as there is no definite chemical compound corresponding to the formula $\text{Al}_2(\text{OH})_6$. It varies in composition from $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ to $\text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$. Consequently it is better to call this pigment hydrous aluminum oxide.

A sample of the material was ignited to constant weight. It was calculated from the amount of water driven off that the formula in this case should be $\text{Al}_2\text{O}_3 \cdot 4.5\text{H}_2\text{O}$.

The commercial method for preparing the hydrous aluminum oxide is that of treating aluminum sulphate in solution with sodium carbonate. This assists in the formation of the hydrate by hydrolysis. The hydrous aluminum oxide pigment thus formed contains some basic aluminum

sulphate. A qualitative test showed the presence of considerable sulphate. The test for the carbonate ion was negative. A slight trace of chloride was found.

Theory of Plastic Flow

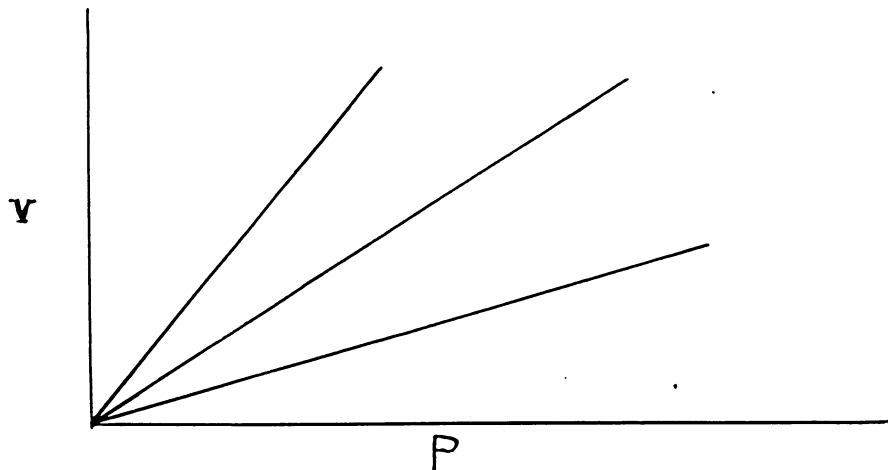
After the classical equation of Poiseuille was put forward in 1842 as a means for calculation of the rate of flow of liquids through narrow tubes, it was not long before various workers turned their attention to the modification which the equation would require in order that it might include within its scope those systems which are not fluids but have also some properties characteristic of both liquids and solids.

The study of the flow of semi-solid(plastic) substances has proved most tantalizing for whereas the flow seemed to be very characteristic, the viscosity as measured by the standard methods was found to vary widely with the shearing stress. Such inexplicable behavior made the results valueless, and progress extremely slow. However, the anomaly was explained by defining a plastic material as one which has characteristics both of a viscous liquid and solid.

The theory of plastic flow can thus be best explained by comparing it with viscous flow, and showing how the two differ. It is quite generally acknowledged that the fundamental law of Poiseuille for viscous liquids holds, as derived from the simple expression:

$$v = Pr \quad (1)$$

where v = the velocity given to a surface by a shearing strength P , the surface being at a distance r from another surface considered at rest, the space between being filled with the viscous fluid. The constant being the fluidity of the liquid. If one were to take the experimental data, substitute in the above formula, and then plot the results obtained, that is, the time rate of displacement against the shearing force, the following family of linear curves, which all start from the origin, would be obtained.

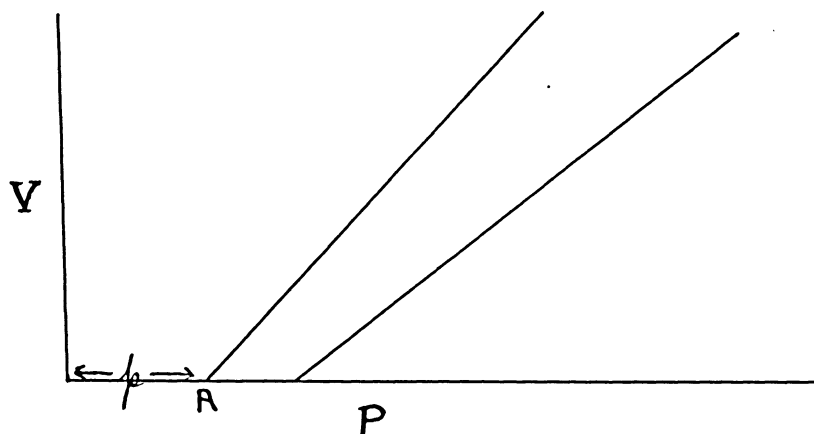


These curves are representative of viscous flow.

For plastic substances, the formula

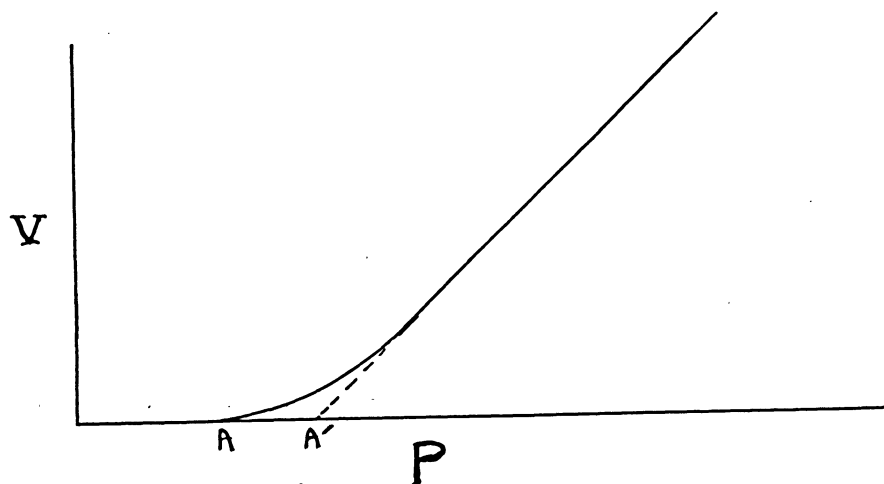
$$v = U (P-p)r \quad (2)$$

has been proposed, where U is the mobility, p is pressure which must be exceeded before flow takes place, and P is the shearing force or pressure. If curves were plotted as above, the following results would be obtained theoretically.



The point A indicates the so-called yield value. Thus we see that with viscous materials the slightest pressure, P , will produce flow, although the rate of flow may be very slow with low pressure applied to the very viscous substances. With plastic materials (according to the simplest theory which seldom holds without complication) the flow is proportional to the pressure in excess of a certain minimum pressure, p , called the yield value, which is required to start flow.

In actual measurements, starting with a low pressure and gradually increasing it, the following type of curve is often obtained.



The point A', an extrapolated point of the straight portion of the curve, indicates the yield point. This point is the subject of much controversy. Whether or not an extrapolation of this nature is permissible in obtaining the yield value is the point in question. The results obtained in starting at a high pressure and lowering it gradually seem to give more accurate and consistent results.

The first coherent attempt to produce a complete equation of flow (2) for systems showing static rigidity was made by Eugene C. Bingham. He showed that a certain amount of pressure is required to overcome the static rigidity, and that under suitable conditions the Poiseuille equation (1) may be applied, provided the pressure term was taken in excess over that amount required to just overcome the static rigidity. Bingham and his co-worker, Green, (9)

(9) Bingham, E. C. and Green, Henry,--Proceedings of the American Society for Testing Materials, 19, 641, (1919)

have pointed out that flow curves plotted with "amount of flow in unit time" as the ordinates and "shearing stress applied" as the abscissae, give for capillaries of different dimensions a family of straight lines, which, when extrapolated backwards over the region of low pressure, all cut the shear-axis at a single point. This point gives a measure of static rigidity of the system. Bingham (10)

(10) Bingham, E. C., "Fluidity and Plasticity" p. 226 (1922)

also points out that this linear relationship holds only at high rates of shear. Fortunately, by using the higher rates of shear, the simple linear relationship can always be obtained. Thus Bingham is of the opinion that the equation

$$v = U (P-p)r \quad (2)$$

can be used to represent the experimental facts. However, if further experiments prove that such is not the case, it will be necessary to use the more complex formulas.

Many American workers, especially ceramists, have made practical use of high shear measurements, and have generally agreed with Bingham that conditions under low shears are too involved to justify serious investigation. Shearer, (11)

(11) Shearer, H. C., Journal of the American Ceramic Society, 11, 542 (1928)

and Reiner (12)

(12) Reiner, Markus, Kolloid Zeitschrift, 39, 80 (1926)

have treated the whole question from the theoretical point of view, basing their work on the postulate of a critical shearing stress which must be exceeded before plastic flow can start at any point, and taking into account the fact

that this critical stress is not attained at different distances from the center of the tube at the same pressure but is attained first at a point nearest the wall. Reiner accounts for the curved portion in the lower regions of the flow curve by considering the solid geometry of the "extrusion figures" when the critical shearing stress has been attained only in part of the cross-section of the tube, so that the material is flowing as a solid plug within an envelope which is being sheared.

The equation of Bingham for plastic flow has been much opposed by various workers. The outstanding man of this group is Winslow H. Herschel, Associate Physicist, United States Bureau of Standards, Washington, D. C., who objects to the determination of yield value by static measurements. Herschel has carried out numerous experiments in connection with his work and has obtained for plastic flow through a capillary a formula of the following nature.

$$I = \frac{d^4 (P - K)n}{q l}$$

where d and l are the diameter and length of the capillary, P is the pressure, and q the rate of flow. The exponent n is a constant of the material, independent of the capillary and increases with concentration. I is another constant of the material which also increases with concentration. K is perhaps an unknown function of a

third constant of the material and of the dimensions of the capillary, but it vanishes at low concentrations and with large capillaries and I should be sufficient to define the consistency of the plastic to which the above equation is applicable.

Williamson offers the following suggestion for various types of flow. Thus viscous flow can be represented:

$$F = Ns$$

Plastic flow

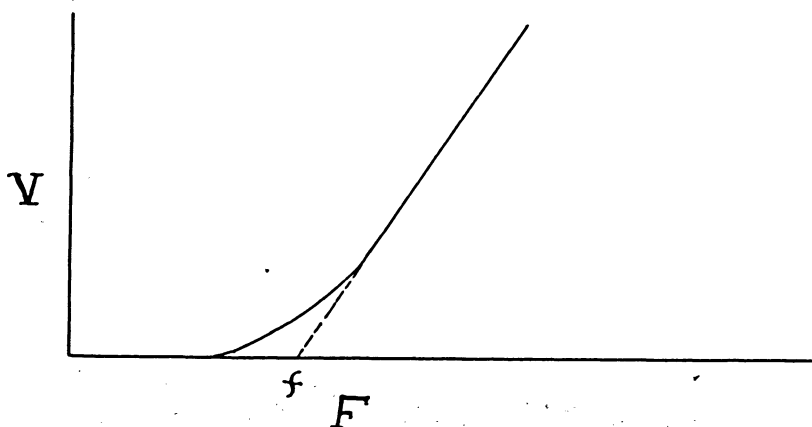
$$F = N_{\infty}s + f$$

Pseudo plastic flow

$$F = N_{\infty}S + f \left(\frac{s}{s + S} \right)$$

where F = shearing stress, S = rate of shear, N = coefficient of viscosity of true fluids, N_{∞} = apparent viscosity at infinite rate of shear for plastic or pseudo plastic flow. N_{∞} is the reciprocal of the mobility constant in Bingham's equation. f = point of intersection with the stress axis of the asymptote to the shear-stress curve. s is a constant determining the curvature of the shear-stress curve when the values of f and N are constant.

The curve obtained is similar to the one shown below.



It was observed by Green (13)

(13) Green, Henry, -Proc. A.S.T.M., 20, part 2, 451, (1920)

by the aid of a microscope that the flow of paint in capillary tubes, at low pressures, the material moved as one solid plug, and that at higher pressures the paint moved in telescopic layers, the inner layers at a much higher velocity than the outer layers.

This observation lead Buckingham (14)

(14) Buckingham, E. - Proc, A.S.T.M., 21, 1154, (1921)

to correct and modify Bingham's earlier equation, thus obtaining the following:

$$\frac{Q}{t} = \frac{\pi g d^4 M}{128 l} \left(P - \frac{4}{3} p + \frac{p^4}{3 p^3} \right) + \frac{d^3 \phi P}{16 l}$$

The last term takes care of viscous slip at the boundaries, it being assumed that there is a very thin lubricating layer of liquid of e and fluidity ϕ between the plastic material and the wall, and that this layer adheres to both the wall and the plastic material.

This equation indicates that below the pressure p the flow, due entirely to slip, increases directly as the pressure. At the pressure p the shearing begins, and the relation between flow and pressure would be shown by a

curve which approximates a straight line at high pressures.

Interesting experimental confirmation of the existence of these two regions of flow was furnished by De Waele (15)

(15) De Waele, A. - Journal of the American Chemical Society, 48, 2760 (1926).

Also--Oil and Color Journal, 6, 33, (1923).

who first accepted and afterwards repudiated Bingham's equation, and ignored Buckingham's. De Waele having found that experimental flow curves are parabolic rather than linear, has questioned the whole treatment, and has shown that his equation, in which pressure is set as proportional to a power of the flow, is valid at very high pressures used by him. Many other workers claim that such an equation fits well the experimental facts even at lower rates of shear.

In concluding this discussion, it might be said, "in the light of present knowledge, it seems quite possible that any one method or equation, for expressing the consistency of a plastic material may not have universal application". Indeed, it seems that each separate class of materials may demand individual treatment.

Experimental - Part II

Study of Inks with the Plastometer

In beginning the work on this problem, an extensive study of the various types of viscometers and plastometers was made. Naturally all the difficulties to be encountered could not be foreseen from the outset. There has only been a limited amount of work done on the study and testing of inks. The incomplete work of Basseches (6, *ibid*), and the work of Perrot and Thiesen (16),

(16) Perrot, G. and Thiesen, R. - "Carbon Black and its Properties and Uses", J. Ind. and Eng. Chem., 12, 324 (1920).

is all that can be found in the literature. The Government Printing Office is at present carrying on work in connection with news inks (17),

(17) "Second Progress Report on Study of News Inks" - by Wehmhoff, B. L. and Clark, D. P. - Technical Bulletin No. 13.

The subject of the present thesis was touched upon by the work of James Ervin (18),

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- (18) Ervin, James - "Colloid Chemistry of Lithographic Ink Constituents" - U. C. Thesis (1930).
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It was for this reason that it was necessary to rely upon the work done with other plastics of a similar nature such as paints, asphalt, and colloidal rubber solutions, for ideas.

At first it was thought that an apparatus which would keep a constant pressure on the plastic during extrusion through a capillary tube would be satisfactory. An apparatus modeled after Bingham and Green's (19),

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- (19) Bingham and Green, - A. S. T. M. 19, Part II, 641-49 (1919).
-

combined viscometer and plastometer had been constructed in the laboratory by a former student, Joseph Jorling. It was found that the results obtained with it were by no means satisfactory. In the first place, the rubber connections were not sufficiently strong to stand the high pressure required for the less mobile inks, consequently it was impossible to get high pressures. In the second place, the yield value obtained was measured statically, which was felt to be undesirable. In the third place, this was a long tedious way of testing inks, therefore it would be unsuitable as a practical control method.

A modified form of a plastometer suggested by the work of Geisy and Arzoomanian (20),

(20) Geisy, P. M. and Arzoomanian, S. A., - Fifth Colloid Symposium Monograph, p. 253 (1923).

was constructed. This instrument consisted of a burette connected by means of a three-way stopcock to a mercury well, and to an ink reservoir fitted with a capillary tube. The burette was calibrated by the mercury method, and was made tall enough to give a pressure in excess of one atmosphere, 82 cm. to be exact. This pressure was found to be insufficient to cause an ink of average mobility to flow through the capillary.

This necessitated another modification which consisted of the use of a closed burette into which mercury was forced against the pressure of a definite volume of trapped air. By so doing a greater pressure range was obtained for extrusion. The general idea of the plastometer can best be obtained from the illustration, Figure 1.

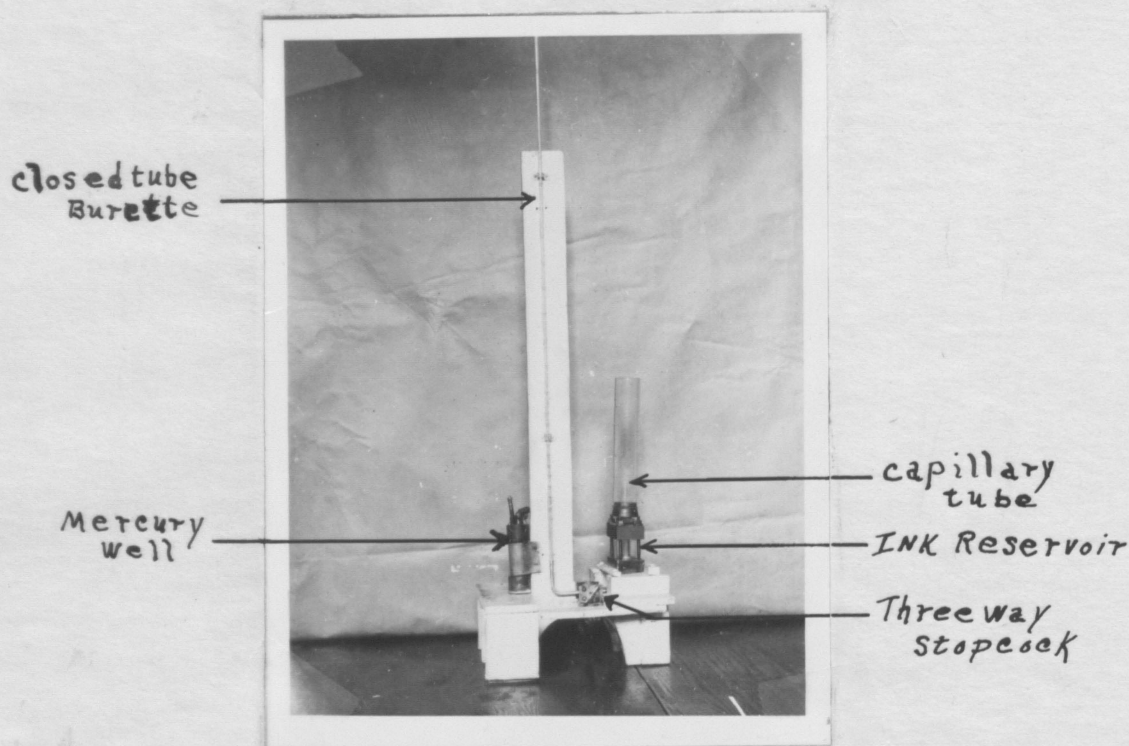
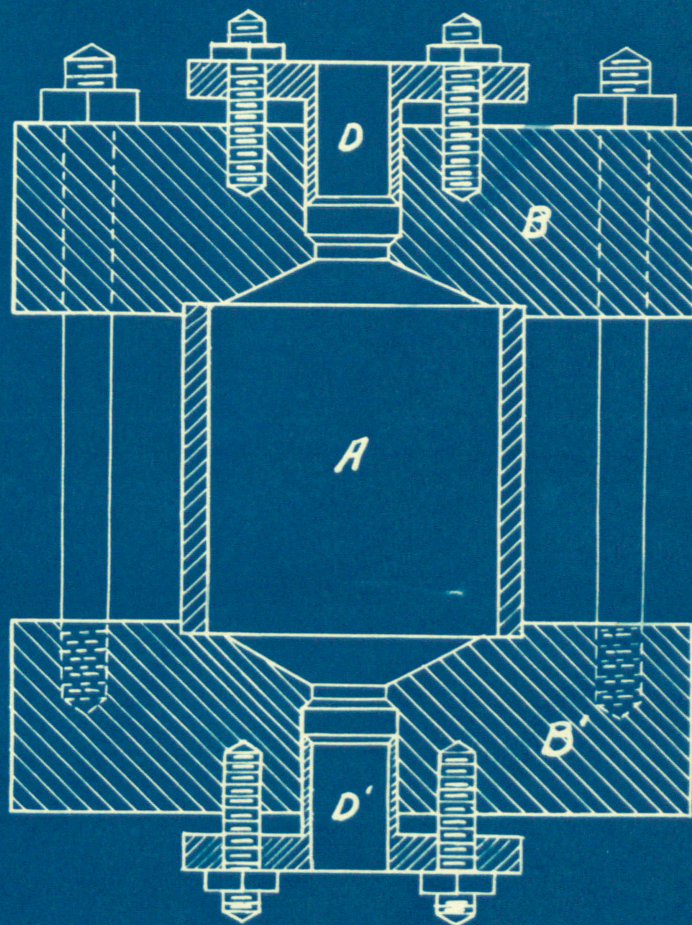


Figure 1.

The closed tube burette was calibrated by the mercury method. The weight-volume relationship of this calibration is given in Table II. The mercury well served as a reservoir from which the mercury could be forced by means of a hand pump into the closed burette. The ink reservoir (see cross-sectional drawing, Fig. 1') consists essentially of a glass cylinder (A), 4.3 cm. in height and 3.7 cm. in diameter and having a volume of 45 c.c. This cylinder (an oil cup of glass) was set between two metal plates (B and B') containing suitable openings for the entrance of mercury and the extrusion of the

Plastic Reservoir
Fig. I'



Cross Section
1" = 1"

plastic through a capillary tube. The glass tube leading from the burette and stopcock was fitted into the stuffing box (D') and tightened into position in the metal plate (B'). The capillary was similarly tightened into place at (D) in the metal plate (B). The advantages of this type of a plastic reservoir permits it to be easily taken apart in filling and cleaning.

It was necessary to calibrate a number of capillaries. It was found desirable to have a series of capillaries of varying radii, so that they could be used over the whole range of ink mobilities. In testing inks having consistencies approaching that of viscous liquids, a capillary having a radius of 1 mm. or less could be used; and for inks of much lower mobility, capillaries of larger radius, 2 mm. or over are required. In calibrating a capillary, the first essential is to determine whether the capillary is of uniform cross section. This was determined by introducing enough mercury to fill the tube with a thread, 5 to 7 cm. in length, and moving it from place to place along the tube and measuring its length in various places by means of a comparator. If the mercury thread showed marked differences in length from place to place, the tube was rejected. Having obtained a capillary of uniform bore, it was cut into the proper length, the ends ground and polished. The length of the tubes was deter-

mined by means of the comparator, four readings being made and the average value used. A suitable method for determining the radius is to fill the capillary with mercury and then expel the mercury into a weighing bottle and weigh. Three determinations of the radius of each capillary were made, and the average taken.

The following table (II') contains the data resulting from the calibration.

Table II'

Dimension of Capillaries used in this study.

Number	Ave. Radius in cm.	Ave. Length in cm.
1	0.1062	10.0931
2	.1457	10.0701
3	.2340	10.0156
4	.2047	10.0165
5 *	.2189	10.2040
6 *	.2077	10.0456

* The inside walls of these capillaries were etched with HF.

The plastometer was suitably mounted on a wooden frame as shown in Figure 1, by means of which it could be easily handled without danger of breaking.

Due to the fact that plastic materials are noticeably affected by temperature changes, it was necessary to make a constant temperature bath. A water bath (see Figure #2))

of galvanized sheet iron having the dimensions 36 x 36 x 46 cm. was obtained.

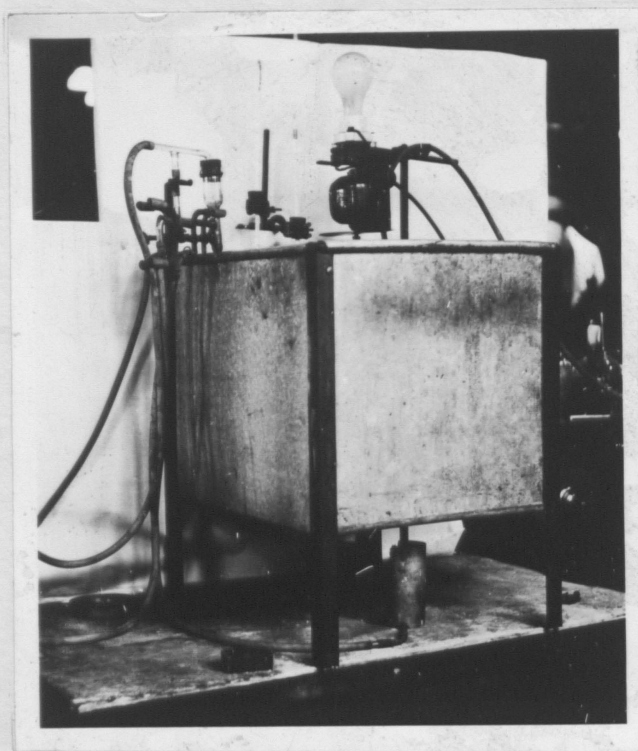


Figure 2.

The size of this bath permitted the entire plastometer to be submerged to a point well above the level of the capillary. A gas thermo-regulator (21)

(21) Findlay, Alexander, - "Practical Physical Chemistry" (1930), p. 59, Longman, Green and Co., New York.

containing toluene and mercury, connected to a small gas burner and regulated to maintain the bath at 25.0 C. proved satisfactory. Agitation of the water was provided by a motor driven stirrer.

Data Sheet for Volume-Pressure Curve

Theoretical pressures- Calibrated volumes

1. Tube Reading cm.	2. Air Pres. in cm. of Hg.	3. Pres. due to Hg. column cm. of Hg.	4. Height of Hg. in reservoir	5. Barometric Pres. in cm. of Hg.	6. Volume Ex- truded	7. Cumulative Volume	8. Summation Pressure cm. of Hg.	9. Average Pressur cm. of Hg.
0	400.8	82	0.456	75.4	0.000	0.000	406.94	354.23
5	318.5	77	0.566	"	1.744	1.744	319.53	288.72
10	262.0	72	0.691	"	1.835	3.579	257.91	235.63
15	223.5	67	0.751	"	1.780	5.359	213.35	196.91
20	194.8	62	0.925	"	1.787	7.146	180.47	166.83
25	172.7	57	1.112	"	1.777	8.923	153.18	141.88
30	155.3	52	1.306	"	1.736	10.659	130.59	120.76
35	141.0	47	1.656	"	1.783	12.442	110.94	102.21
40	128.7	42	1.821	"	1.818	14.260	93.48	85.85
45	118.6	37	1.985	"	1.789	16.049	78.21	71.32
50	110.0	32	2.156	"	1.795	17.844	64.44	61.86
52	106.9	30	2.224	"	.701	18.545	59.28	57.14
54	104.7	28	2.294	"	.702	19.247	55.01	51.77
56	101.3	26	2.362	"	.700	19.947	49.54	47.20
58	98.7	24	2.428	"	.699	20.647	44.87	42.63
60	96.3	22	2.498	"	.699	21.346	40.40	38.17
62	93.9	20	2.564	"	.700	22.057	35.94	33.80
64	91.7	18	2.632	"	.700	22.758	31.67	29.58
66	89.6	16	2.698	"	.704	23.562	27.50	25.46
68	87.6	14	2.778	"	.708	24.271	23.42	21.38
70	85.6	12	2.846	"	.708	24.980	19.35	17.42
72	83.7	10	2.914	"	.718	25.698	15.39	13.36
74	81.8	8	3.066	"	.718	26.416	11.33	
82	74.5	0	3.217	"	2.736	29.152	-3.217	

In using this plastometer to test an ink it was necessary to work out a volume-pressure table (Table II) characteristic of the apparatus. In column (2) of this table the pressure due to compressing the entrapped air was given in cm. of mercury. In column (3) the pressure due to the height of the mercury column was given. The sum of these two pressures gives the total pressure causing flow. This total pressure was opposed by one atmosphere of air, column (5), and the hydrostatic head of mercury (4) which flows into the plastic reservoir from the burette as the ink was extruded. The data in Table II were plotted in Figure 3 and labeled the volume-pressure curve. In practice, the average pressure causing extrusion of a given volume of ink can be read directly from the curve. The value thus obtained must be corrected for barometric pressure and the density of the ink.

The procedure in testing an ink with this instrument was as follows: The apparatus was first cleaned and the mercury level adjusted. The ink to be tested was run over the ink mill twice to restore as nearly as possible its original mobility. It is a known fact among ink manufacturers and users that inks tend to acquire a "set" or "false body" upon standing, probably due to flocculation of the pigment. This phenomenon can be reversed by regrinding or working the ink on the slab, unless chemical livering has taken place.

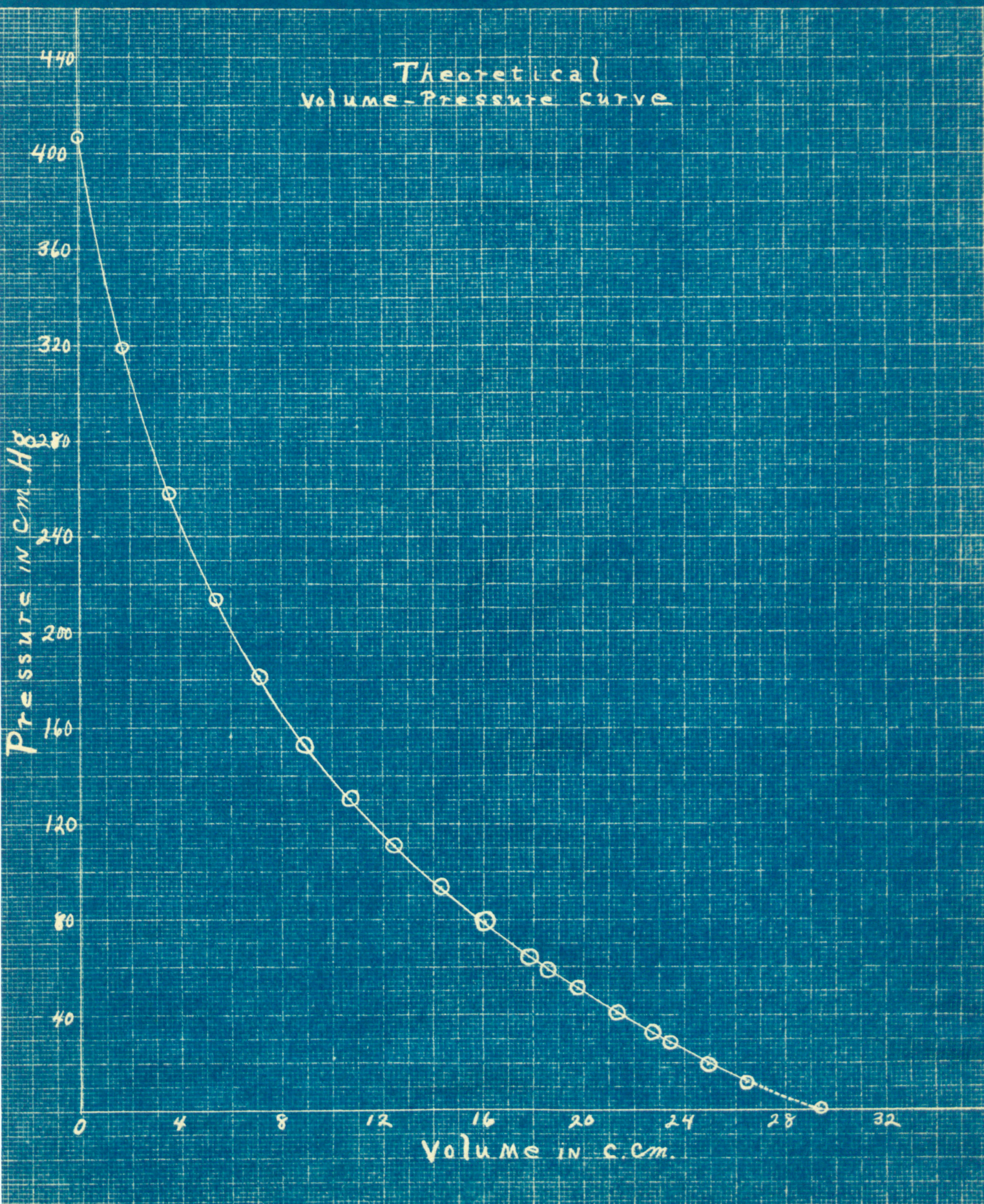


Figure 3.

The glass cylinder (A - Fig. I') was next put in place on the lower metal plate of the reservoir, and filled with ink that had been previously milled. In doing this, great care was taken to prevent the introduction of air bubbles or air pockets. The upper metal plate of the ink reservoir containing the capillary was next put in place. In tightening this plate into position, the pressure applied by the nuts on the four corners had to be uniform to prevent the breakage of the glass cylinder. A rubber stopper was placed on the extended portion of the capillary tube and a large glass cylinder was placed over it, (see Figure 1), to prevent the extruded ink from falling back into the water bath. The apparatus was then placed in the bath and allowed to remain thirty minutes.

After the plastic had attained a constant temperature (25.0 C.), the mercury in the well was forced by means of a hand pump into the burette. The burette was connected by means of the three-way stopcock with the ink reservoir. Enough mercury was permitted to flow through into the ink reservoir to force the plastic to the top of the capillary tube. The burette was again connected with the mercury well and the mercury forced to a height of one cm. above the starting point (zero mark). The stopcock was then opened, connecting the burette with the ink reservoir. As the top of the mercury column passed the zero mark on the burette, a stopwatch was started and the time of flow in seconds was

recorded for every 5 cm. fall of the mercury column from zero down to the 50 cm. mark. Thereafter, the time was taken for every 2 cm. fall of the mercury column.

Then from columns (1) and (6), Table II, the volume extruded, and the average pressure causing flow, column (9), could be obtained. The data for the pressure rate-of-flow diagrams were obtained by using the volume extruded in c.c., and the time in seconds required for the extrusion. That is, by dividing the volume extruded by the time, the ratio dv/dt could be obtained. This value could then be plotted against the corrected average pressure to give the typical pressure-rate-of-flow diagram.

The preliminary run with this closed burette plasto-meter was made with an offset process black ink of the consistency used on the press. The results of this run are given in Table III, and the data of columns (5) and (6) were used in plotting the pressure-rate-of-flow diagram, Figure 4. The rate of flow dv/dt (column 5), was plotted as ordinates, and the average pressure values as abscissae. The results thus obtained indicated that the instrument could be used satisfactorily in testing lithographic inks.

The Effect of the Temperature on Inks

A series of experiments was next carried out in which the effect of temperature upon the rate of flow of an ink was studied. All other variables were kept as nearly constant as possible and the temperature varied from 15 to 35 C.,

An Ault and Wiborg Offset Black Ink was used in this series of tests. This ink, as it was taken from the container, was too stiff to be used on the press. Therefore 500 grams of the ink was reduced with 112 grams of boiled linseed oil (for physical properties of this oil see Table I) to the approximate consistency as used on the press. Runs were made at 15, 25, and 35 C. The results are given in Table IV, and plotted in the form of a curve in Figure 5.

Table III

Preliminary Run with Closed Tube Plastometer

Conditions:-----Temperature----25 C.
 Pressure-----744 mm.
 Density of ink--1.124
 Capillary #3 R----0.2340 cm.
 L---10.0156 cm.

1. Tube Reading	2. Time in Seconds	3. dt	4. dV	5. dV/dt	6. Average Pressure
0-5	2	2	1.744	0.871	353.2
10	4.8	2.8	1.835	.655	287.7
15	8.6	3.8	1.780	.470	234.6
20	14.2	5.6	1.787	.324	195.9
25	20.6	6.4	1.777	.278	166.8
30.75	31	10.4	2.130	.206	140.4
42	60	29	3.930	.136	107.6
52	109	49	3.570	.073	73.2
62	221	112	3.502	.031	47.5
72	900	679	3.467	.005	25.7

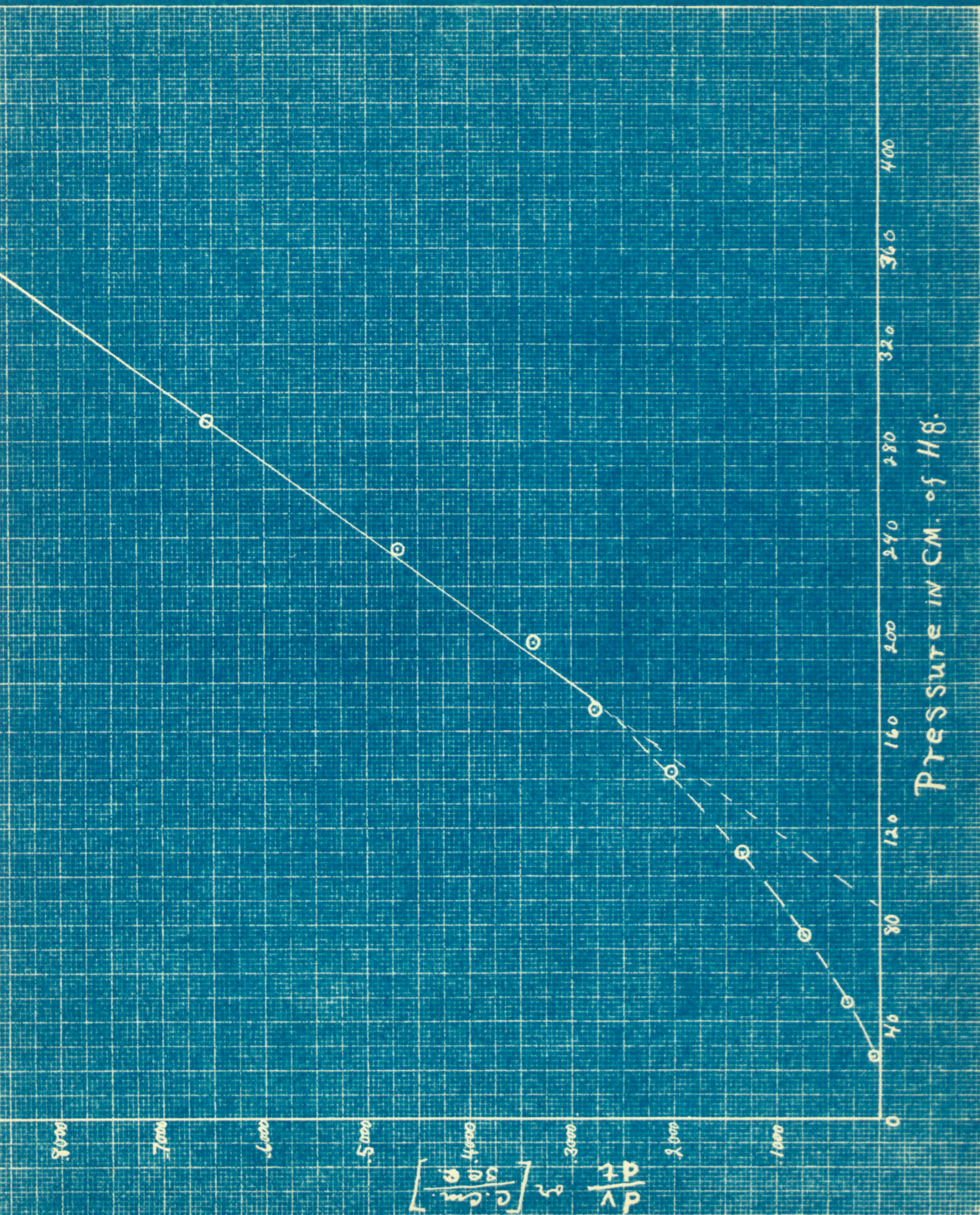


Figure 4.

Relation of Capillary Size to the Mobility of Inks

A study was next made of the effect of different sizes of capillaries upon the plastic properties of inks. Bingham (19, *ibid.*) recommends in the description of his variable-pressure plastometer that at least four capillaries should be available so that the effects on the rate of flow, due to the change of length and radius of the capillary may be observed. Reiger and Glasser (22),

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- (22) Reiger, R. and Glasser, - *Ann. Physik.*, 22, 694 (1907)
Also Bingham, E. C., - "Fluidity and Plasticity",
p. 239, McGraw-Hill Book Co., N. Y. 1922.
-

investigated the limits of the radius of capillary tubes with various concentrations of colophony suspended in turpentine. They found that with an 80% suspension of colophony the lower limits of the radius of the capillary was 0.100 cm., with an 85% mixture it was 0.576 cm., and with a 90% it was 1.019 cm.

In this investigation, capillaries of three different sizes were used. All other variables were maintained as nearly constant as possible. The data is given in Table V, and plotted in Figure 5'. It can be seen from these results that the optimum radius for the study of lithographic inks is in the neighborhood of 0.2340 cm. Thus the largest capillary tube can be used in the testing of still heavier inks, but this cannot be said of the two smaller ones.

Table IV

The Effect of Change of Temperature on Inks

Run 1.

Conditions:-----Temperature-----15 C.
 Pressure-----740 mm.
 Density of ink--1.120
 Radius of capillary--0.2340 cm.
 Length of capillary--10.0156 cm.

1. Tube Reading	2. Time in Seconds	3. dt	4. dV	5. dV/dt	6. Corrected Ave. Pres.
0-5	6.5	6.5	1.744	0.268	351
10	16	9.5	1.835	.193	282
15	28.5	12.5	1.780	.143	230
20	44	15.5	1.787	.115	191
25	64.5	20.5	1.777	.086	161
30.75	95.1	30.6	2.130	.060	127
42	193.5	98.4	3.930	.040	103
52	367	173.5	3.570	.021	71
62	830	463.0	3.502	.008	43
72	3660	2830	3.467	.001	25

Run 2.

Conditions same as above, except T---25 C.

0-5	3.4	3.4	"	0.515	"
10	8	4.6	"	.395	"
15	14	6	"	.296	"
20	21.5	7.5	"	.238	"
25	31	9.5	"	.187	"
30.75	45.2	14.2	"	.135	"
42	89	43.8	"	.090	"
52	165	76	"	.047	"
62	355	190	"	.018	"
72	1960	1605	"	.002	"

Run 3.

Conditions same as above, except T---35 C.

0-10	4	4	3.579	.895	318.7
20	10.4	6.4	3.567	.560	213.2
30.75	20.6	10.2	3.907	.382	153
42	39.5	18.9	3.930	.208	103
52	73.5	34	3.570	.105	71
62	158.5	85	3.502	.041	43
72	960	801.5	3.467	.004	25

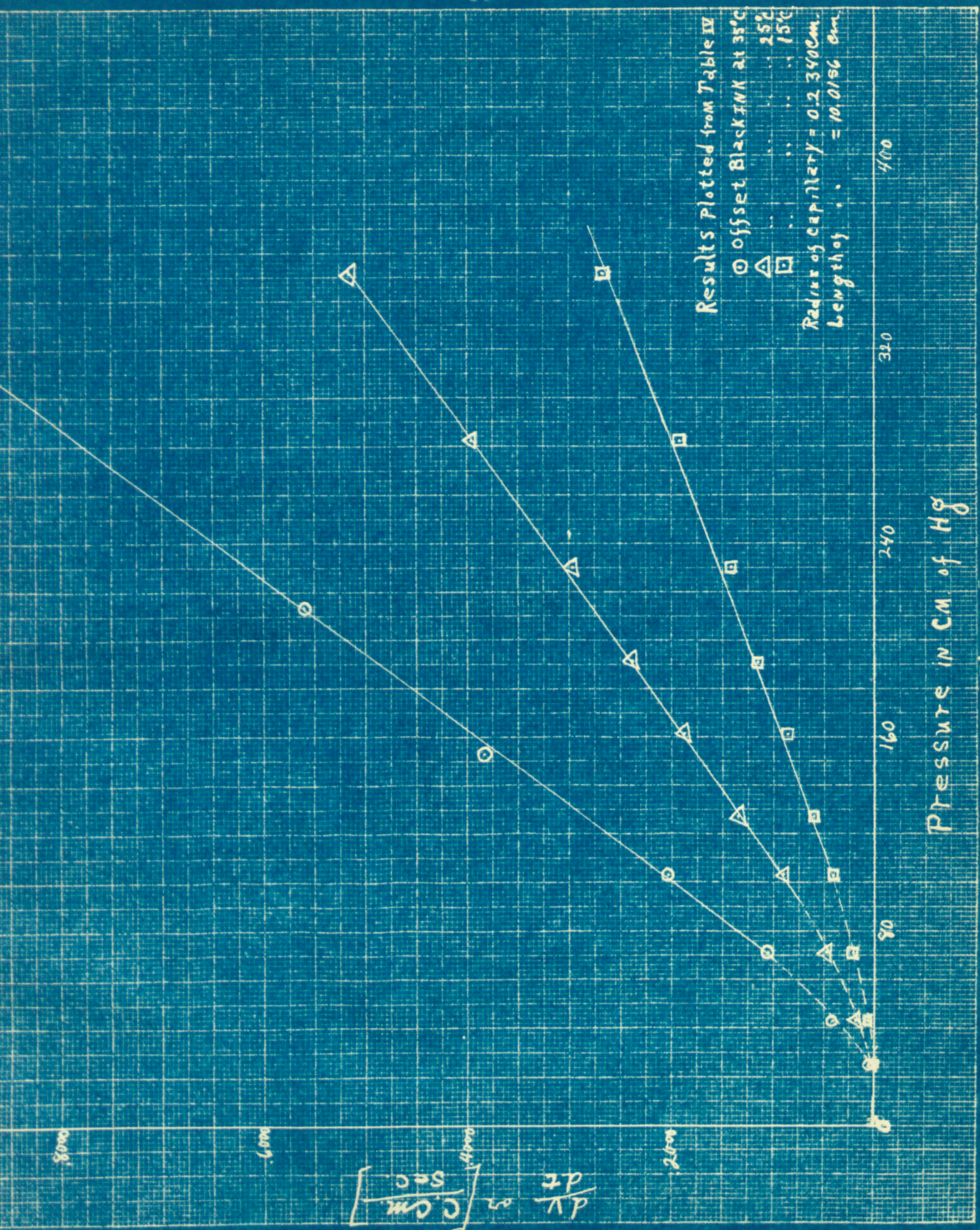


Figure 5.

Table V.

Relation of Capillary Size to Mobility of Inks

Run 1.

Conditions:-----Temperature-----25 C.
 Pressure-----750 mm.
 Density of ink---1.120
 Radius of capillary--0.1062 cm.
 Length of capillary-10.0931 cm.

1. Tube Reading	2. Time in Seconds	3. dt	4. dV	5. dV/dt	6. Corrected Ave. Pres.
0-5	52.1	52.1	1.744	0.0335	350
10	129.1	77.0	1.835	.0238	281
15	231.4	102.3	1.780	.0174	229
20	367	125.6	1.787	.0143	190
25	546.2	179.2	1.777	.0099	160
30.75	834	287.8	2.130	.0074	126
42	1832	998.0	3.930	.0039	102
52	4140	2308.0	3.507	.0015	70

Run 2.

Conditions:--Same as above except--

Pressure----745 mm.
 Radius of capillary--0.1457 cm.
 Length of capillary-10.0701 cm.

0-5	13	13	1.744	0.1340	350.5
10	32.2	19.2	1.835	.0955	281.5
15	57	24.8	1.780	.0718	229.5
20	90.2	33.2	1.787	.0539	190.5
25	133.2	43	1.777	.0413	160.5
30.75	199	65.8	2.130	.0324	126.5
42	409	210	3.930	.0187	102.5
52	833	424	3.570	.0085	70.5
62	1820	987	3.502	.0035	42.5
72	4215	2395	3.467	.0015	24.5

Table V (Cont.).

Run 3.

Conditions:--Same as above except--

Pressure----740 mm.

Radius of capillary--0.2340 cm.

Length of capillary-10.0156 cm.

0-5	3	3	1.744	0.558	351
10	7.3	4.3	1.835	.429	282
15	12.8	5.5	1.780	.324	230
20	19.8	7	1.787	.255	191
25	29.2	9.4	1.777	.190	161
30.75	45	15.8	2.130	.135	127
42	88.6	43.6	3.930	.090	103
52	163	74.4	3.570	.048	71
62	335	162	3.502	.022	43
72	1900	1565	3.467	.002	25

Comparison of results obtained with smooth and etched capillaries.

The next work was concerned with the study of the use of etched capillaries. This investigation was suggested by the work done by Blair and Crowther (23),

(23) Blair, G. W. S., and Crowther, E. M., Journal of Physical Chemistry, 33, 321 (1929).

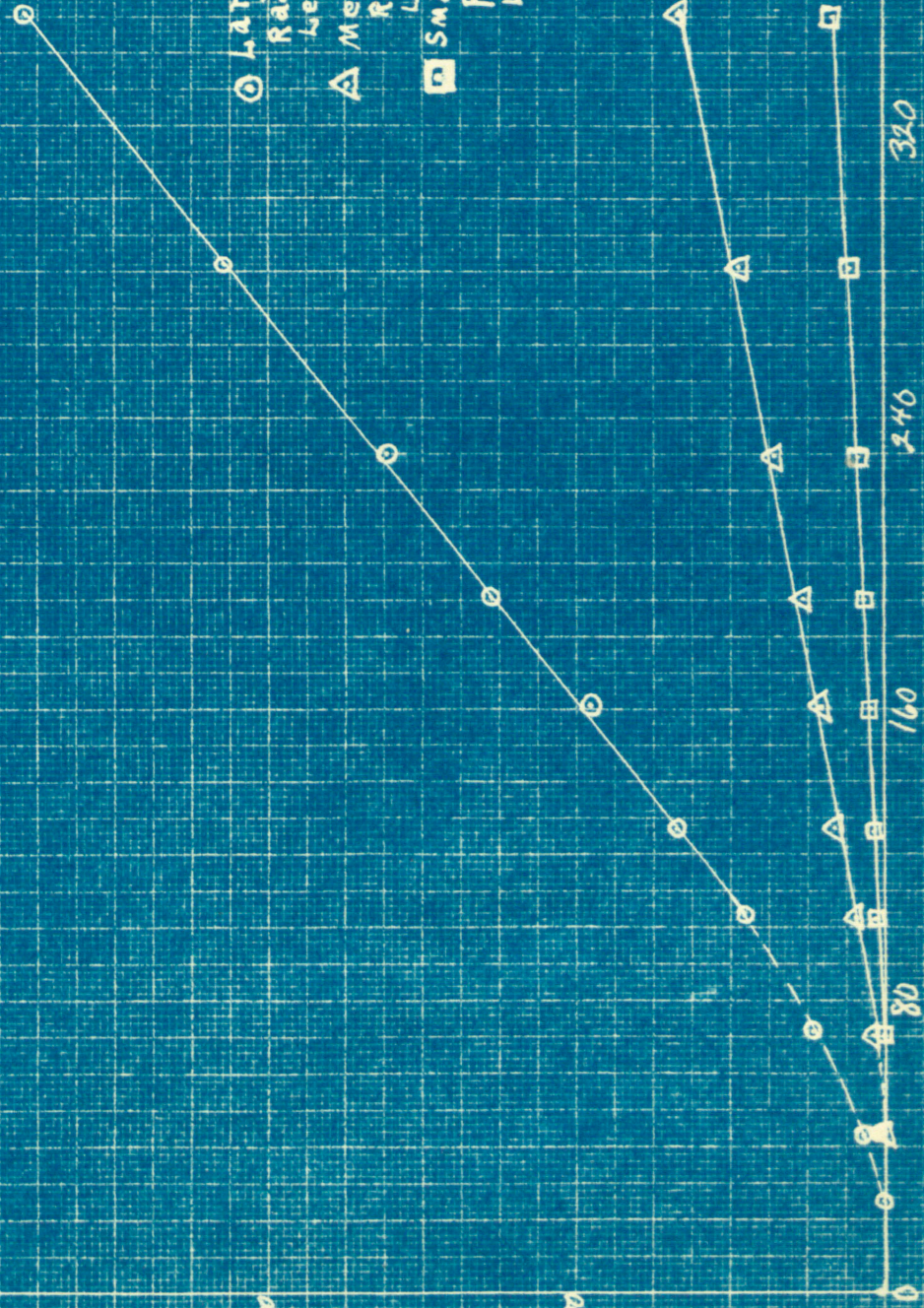
on soil pastes. By starting with a low pressure and gradually increasing it, they found there were four separate stages in the flow of the clay paste, depending on the pressure. These stages as described by them were as follows:

8000

6000

2000

$$\frac{dv}{dt} \propto \left[\frac{c \text{ cm}}{\text{sec}} \right]$$



○ Large capillary

Radius = 0.2340 cm.
Length = 10.0156 cm.

△ Medium capillary

Radius = 0.1459 cm.
Length = 10.0701 cm.

□ Small capillary

Radius = 0.1062 cm.
Length = 10.0931 cm.

Results Plotted from Table V
○ Offset Black ink Large capillary
△ " " " Medium
□ " " " Small

Pressure in cm. of Hg.

Figure 5.

In Stage I there was no motion of the paste until a well defined critical shearing stress (yield value) was reached and exceeded.

In Stage II the clay paste moves as a rigid plug through the capillary and the flow is linear over a considerable range.

In Stage III the clay flows as a central plug within a stream-line shell of increasing thickness and the flow curve bends rapidly upward. The plug flow in Stage II and the mixed plug and concentric cylinder flow in Stage III are responsible for the curvature of the lower part of the curve in the pressure flow diagram.

In Stage IV the flow of the paste at the high rates of shear is stream-line throughout and the upper part of the curve is rectilinear.

They found additional evidence of the essential physical difference between the types of flow in Stages II and IV by experimenting with tubes which had been roughened internally by means of hydrofluoric acid. The roughening of capillary would be expected to interfere seriously with the thin envelope or film which tends to lubricate the plug flow and mixed flow in Stages II and III, but to have very little effect on the concentric cylinder flow of Stage IV.

This was found to be true. They found in the stream-line region that the points for the roughened capillary approximated very closely the results obtained by the smooth one. In Stage II as was expected there was a wide

divergence and the rate of flow for a given pressure was greatly reduced. Thus it follows that plug flow is inhibited to a certain extent by the etched walls of the capillary.

The study of inks is analogous to that of clay pastes in several respects. The pigment takes the place of clay, and the linseed varnish serves as the vehicle. It is a known fact that inks working satisfactorily on a lithographic press contain from 6 to 15% of water (24),

(24) Beecher, B. K., "Hygroscopic Properties of Inks",
U. C. Thesis, p. 36 (1929).

and for this reason it was considered advisable to study the effects of water upon the properties of a lithographic ink. Hence it can be seen that in the case of the saturated inks, the possibility of plug flow would be increased due to the lubricating effect of the varnish, or to the water film, or to an emulsion of the two.

It was for this reason considered advisable to make a study of the type of flow obtained by the use of smooth and etched capillaries. It was hoped by the use of the etched capillary and this type of instrument, in which the flow starts at high rates of shear and then diminishes, that the telescopic flow taking place at the high rates of shear should continue to take place at the lower rates. (See Table II', capillary #5)

This etched capillary was made by means of hydrofluoric acid. This capillary had about the same radius as the smooth one (capillary #4). The ink used in this study contained 35% hydrous aluminum oxide and 65% #1 varnish (for physical properties see Table I). The materials were mixed and thoroughly ground on an ink mill. Immediately after preparation a sample of the ink was put in the plastometer and extruded through the smooth capillary. It was next run through the etched capillary. The conditions and results are given in Table VI.

The next day a sample of the same ink was run over the mill twice and then saturated with water by working water into it on the ink slab. A sample of this ink was extruded through the smooth capillary, and in the afternoon a sample of the ink saturated in the morning was run through the etched one. The conditions and results are given in Table VII. The results of both Tables VI and VII are plotted in Figure 6.

It can be seen from the pressure-rate-of-flow diagram (Figure 6) that the dry inks show the greater mobility when extruded through the etched capillary, as indicated by the slope of the curve. This can be accounted for by the fact that the etched capillary has the larger radius.

However, in the case of the saturated ink the mobility as indicated by the slope of the curve obtained with the smooth capillary is greater than that of the etched capillary. This is just the opposite of the results obtained in the case of the dry ink. The explanation of this pheno-

Table VI Comparison of Results Obtained with Smooth and Etched Capillaries.

Run 1.

Conditions:-----

Temperature-----25 C. Pressure-----742 mm.
Density of ink---1.1915 Radius of capillary---0.2047 cm.
% water in dry ink---4.62 Length of capillary--10.0165 cm.
This run was made with the smooth capillary and dry ink.

1. Tube Reading	2. Time in Seconds	3. dt	4. dV	5. dV/dt	6. Corrected Ave. Pres.
0-5	4.8	4.8	1.744	0.364	353
10	11.3	6.5	1.835	.282	284
15	19.2	7.9	1.780	.225	232
20	29.6	10.4	1.787	.171	193
25	41.5	11.9	1.777	.149	163
30	54.4	12.9	1.736	.125	141
35	72.8	18.4	1.783	.0969	121
40	96.4	23.6	1.788	.0757	103
45	127.7	31.3	1.789	.0572	86
50	167.4	39.7	1.795	.0452	71
52	187.4	20.0	.701	.0350	62
56	237.6	29.8	.700	.0285	52
60	307.8	39.0	.699	.0179	42
64	414.6	63.8	.699	.0109	33
70	855	230.0	.704	.0030	20

Run 2.

Conditions other than the above:-----

Radius of capillary---0.2189 cm.
Length of capillary--10.2040 cm.
This run was made with the etched capillary and dry ink as above.

0-5	3.3	3.3	1.744	0.530	353
10	7.8	4.5	1.835	.405	284
15	13.4	5.6	1.780	.319	232
20	20.8	7.4	1.787	.241	193
25	30.2	9.4	1.777	.189	163
30	41.4	11.2	1.736	.155	141
35	55.8	14.4	1.783	.124	121
40	75.2	19.4	1.788	.0922	103
45	99.6	24.4	1.789	.073	86
50	131.8	32.2	1.795	.056	71
52	148.2	16.4	.701	.043	62
56	189.4	22.6	.700	.031	52
60	248	33.4	.699	.021	42
64	338	52.6	.699	.013	33
70	755	235	.709	.003	20

Table VII Continuation of Same Test as in Table VI.

Run 3.

Conditions:-----

Temperature-----25 C. Pressure-----750 mm.
 Density of ink---1.1995 Radius of capillary---0.2047 cm.
 % water in sat. ink--25.25 Length of capillary--10.0165 cm.
 This run was made with the smooth capillary and
 saturated ink.

1. Tube Reading	2. Time in Seconds	3. dt	4. dV	5. dV/dt	6. Corrected Ave. Pres.
0-5	7.6	7.6	1.744	0.231	352.2
10	18.6	11.0	1.835	.167	283.2
15	33.0	14.4	1.780	.124	231.2
20	54.0	21.0	1.787	.084	192.2
25	84.8	30.4	1.777	.058	162.2
30	125.4	40.6	1.736	.043	140.2
35	186.8	61.4	1.783	.029	120.2
40	286	99.4	1.788	.018	102.2
45	451	165	1.789	.0108	85.2
50	767	316	1.795	.0057	70.2
52	924	157	.701	.0044	61.2
54	1275	351	.702	.0020	55.2
56	1685	410	.700	.0014	51.2
58	2190	505	.700	.0014	46.2
60	3090	900	.704	.0007	41.2

Run 4.

Conditions other than the above:-----

Radius of capillary---0.2189 cm.
 Length of capillary--10.2040 cm.
 This run was made with the etched capillary and
 saturated ink.

0-5	8.7	8.7	1.744	0.201	352.2
10	21.4	12.7	1.835	.145	283.2
15	39.0	17.6	1.780	.102	231.2
20	64.8	25.8	1.787	.069	192.2
25	106.4	41.6	1.777	.043	162.2
30	170.8	64.4	1.736	.027	140.2
35	280.6	109.8	1.783	.016	120.2
40	485	204.4	1.788	.0088	102.2
45	860	375	1.789	.0048	85.2
50	1565	705	1.795	.0025	70.2
52	1995	430	.701	.0016	61.2
54	2558	563	.702	.0012	55.2
56	3310	752	.700	.0009	51.2
58	4275	965	.700	.0007	46.2
60	6060	1785	.704	.0004	41.2

Results Plotted from tables III & VII

- Etched capillary and dry ink
- △ Smooth
- Etched
- × Saturated ink

Dimensions of Etched capillary

Radius = 0.2189 cm.

Length = 10.2040 cm.

Dimensions of smooth capillary

Radius = 0.2049 cm.

Length = 10.0165 cm.

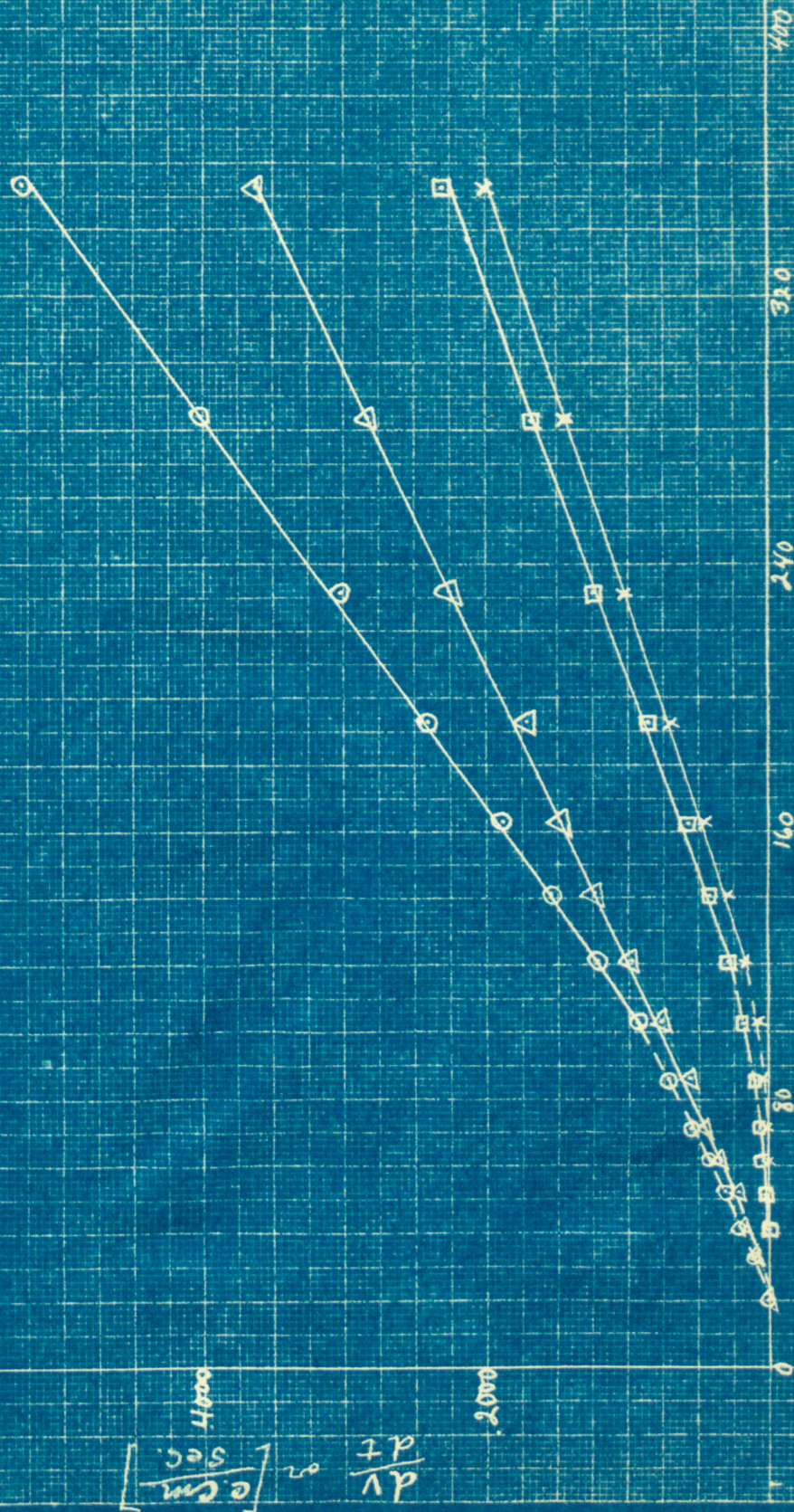


Figure 6.

menon is that after being saturated in the morning, and one portion run through the smooth capillary, the remaining portion of saturated ink was allowed to stand about four hours before being run through the etched capillary in the afternoon. This sample was worked on the slab in the same manner as the previous sample, but during this time the ink had acquired a certain amount of irreversible "set" which could not be removed by working. Consequently, as the curves show, with the etched capillary, it was less mobile. Additional work showed that this set was due to soap formation which is accelerated by the presence of water.

A Comparative Test of the Properties of Long and Short Inks.

The next work was concerned with the comparison of two inks of entirely different physical properties. This comparison was carried out by the use of the empirical finger tests and by extrusion through the plastometer. The materials were chosen with the idea that the one should be a short and the other a long ink.

The formulas of the two inks are as follows:

Long Ink

Hydrous Al_2O_3	-----40%
#1 Varnish	-----60%

Short Ink

Hydrous Al_2O_3	-----43%
#0000 Varnish	-----52%
#7 Varnish	----- 5%

The physical and chemical properties of materials used in the preparation of these inks can be found in Table I.

The result of the finger test comparison was as follows: The long ink pulled into threads 3 to 4 inches in length. The short ink would not pull into threads over one-half inch long. The long ink offered the least amount of resistance to the finger when it was moved around in a small smear of the ink. There was no appreciable difference in tack.

The two inks were then run through the plastometer. The conditions and results obtained with the plastometer with the long and the short inks run dry are given in Table VIII.

A comparison of the two inks after being saturated with water was next made. The finger tests showed that the length and mobility of the long ink had been reduced. It would pull into threads of only about 2 inches in length, about half the length obtained with the dry ink. The tack was reduced slightly but not in the same proportion as the length. The short ink was made even a little shorter, having its mobility and tack also reduced.

From previous experience with the plastometer it was considered advisable to run the ink immediately after saturation. Thus the two inks were run directly after being saturated with water. The conditions and results are given in Table IX. The data in both Tables VIII and IX are plotted in Figure 7.

Table VIII Comparative Test of a Long and Short Ink.

Run 1--Long Ink.

Conditions:-----

Temperature-----25 C.

Pressure-----739 mm.

Density of ink---1.237

Radius of capillary---0.2189 cm.

% water in dry ink---4.26

Length of capillary--10.2040 cm.

1. Tube Reading	2. Time in Seconds	3. dt	4. dV	5. dV/dt	6. Corrected Ave. Pres.
0-5	6.8	6.8	1.744	0.2565	353.5
10	16.4	9.6	1.835	.1912	284.5
15	29.0	12.6	1.780	.1410	232.5
20	44.8	16.8	1.787	.1062	193.5
25	67.2	22.4	1.777	.0793	163.5
30	95.6	28.4	1.736	.0612	141.5
35	139.2	43.6	1.783	.0448	121.5
40	197.2	58.0	1.788	.0324	103.5
45	275.4	78.2	1.789	.0229	86.5
50	397.8	122.4	1.795	.0147	71.5
52	469	71.2	.701	.0098	62.5
56	682.8	125	.700	.0056	52.5
60	1143	287	.699	.0024	42.5
64	3180	1582	.699	.0005	33.5

Run 2--Short Ink.

Conditions other than the above:-----

Pressure-----744 mm.

Density of ink---1.241

% water in dry ink---6.22

0-5	7.2	7.2	1.744	0.2445	353
10	18.2	11.0	1.835	.1630	284
15	34.8	16.6	1.780	.1075	232
20	64.6	29.8	1.787	.0600	193
25	121.8	57.2	1.777	.0311	163
30	241.2	119.4	1.736	.0145	141
35	612.8	371.6	1.783	.0048	121
40	7080	6467.2	1.788	.0003	103

Table IX Comparative Tests of a Saturated Long and
Short Ink.

Conditions:-----

Temperature-----25 C. Pressure-----739 mm.
Density of ink---1.245 Radius of
% water in saturated ink--27.2 capillary---0.2189 cm.
Length of capillary--10.2040 cm.
This run was made with the long ink saturated.

1. Tube Reading	2. Time in Seconds	3. dt	4. dV	5. dV/dt	6. Corrected Ave. Pres.
0-5	9.7	9.7	1.744	0.1790	353.5
10	24.1	14.4	1.835	.1278	284.5
15	43.0	18.9	1.780	.0941	232.5
20	70.8	27.8	1.787	.0643	193.5
25	110.8	40.0	1.777	.0444	163.5
30	165.6	54.8	1.736	.0317	141.5
35	247.8	82.2	1.783	.0217	121.5
40	379.2	171.4	1.788	.0104	103.5
45	586.4	207.2	1.789	.0086	86.5
50	991.2	404.8	1.795	.0044	71.5
52	1240	248.8	.701	.0028	62.5
56	2070	490	.700	.0014	52.5
60	3750	1010	.699	.0007	42.5
64	7680	1390	.699	.0003	33.5

Run 4.

Conditions other than the above:-----

Pressure-----744 mm.
Density of ink---1.250
% water in saturated ink---31.52
This run was made with the short ink saturated.

0-5	11.8	11.8	1.744	0.1478	353
10	34.4	22.6	1.835	.0814	284
15	81.2	46.8	1.780	.0380	232
20	177.4	96.2	1.787	.0186	193
25	965	787.6	1.777	.0023	163
30	4380	3415.0	1.736	.0005	141

Results Plotted from tables VIII & IX

- Long INK Run dry
- △ .. Saturated
- Short INK Run dry
- x .. Saturated

3000

2000

1000

$\frac{7p}{1p}$

400

320

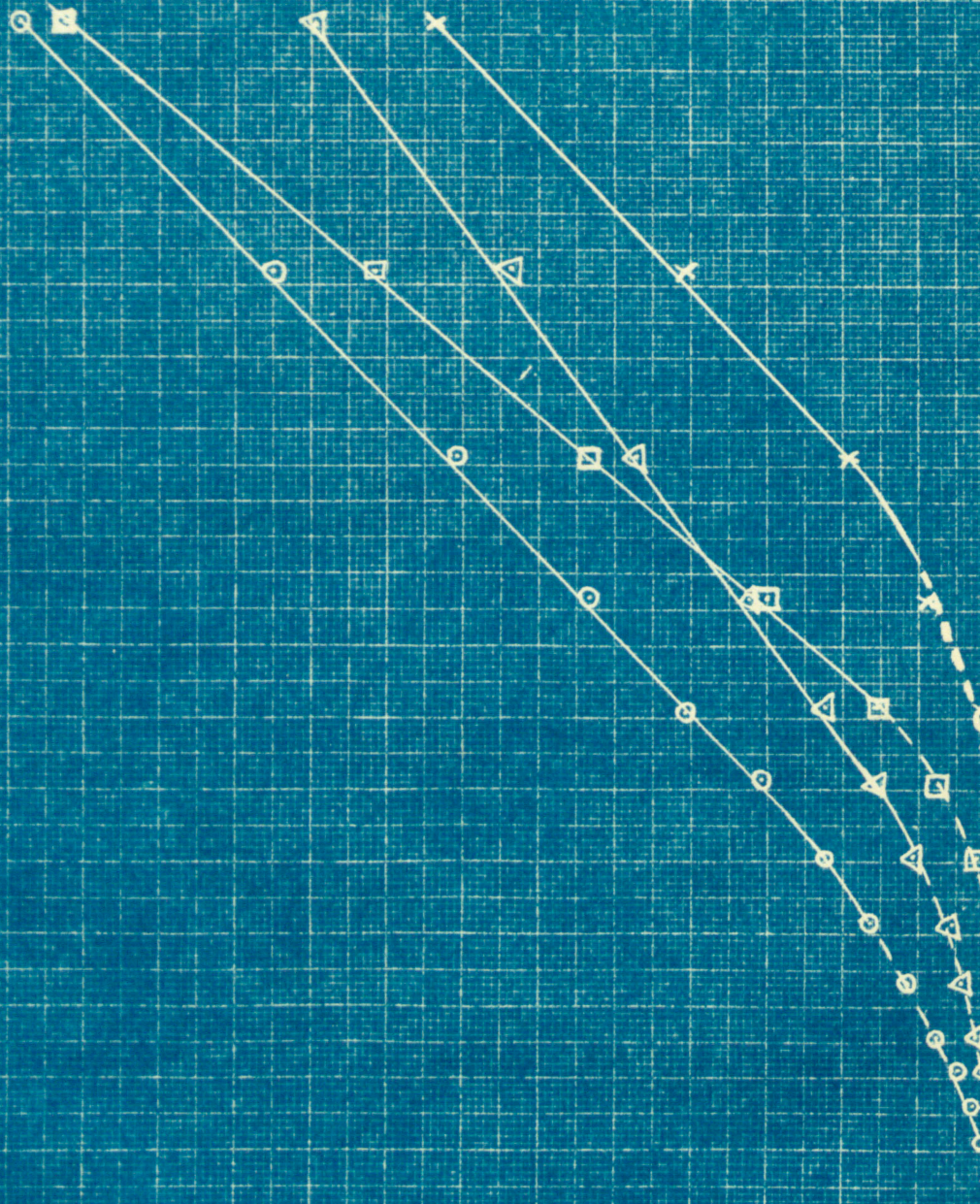
240

160

80

Pressure in CM. of Hg.

Figure 7.



In a study of the curves in Figure 7, it can be observed that the original long ink is the most mobile. The short ink ranks next in mobility at the high rates of shear, but at the lower rates of shear it appears less mobile. This is probably a fallacy. The short ink having a high yield point appears less mobile than it is in reality. The saturated long ink is next in mobility, while the short saturated ink is obviously the stiffest or most rigid of the group.

It can readily be seen that the yield value of an ink is indicative of its length. The graphical results indicate that the ink which has the lowest yield point is the longest. The dry long ink having a length of about 4 inches had a yield point of 33.5 cm. of mercury. The saturated long ink was next, being longer than the dry short ink and had a value of 42.5 cm. The yield value of the short ink which pulled into threads about one-half inch in length was 103 cm., while that of the same ink saturated was 141 cm. of mercury.

In general it can be said that the plastometric measurement gives information concerning the body of an ink. The slope of the pressure-rate of flow curve indicates whether a given ink is soft or rigid. The yield point gives information concerning the length or shortness of an ink.

It was unfortunate that the results obtained with this apparatus gave no information concerning tack. It will be remembered that in making tack measurements by the finger method, one rubs a small smear of the ink out into a thin

film and then notes the resistance to splitting of the thin film of ink when the finger is quickly lifted. This procedure was thought to be comparable to the flow of an ink through a capillary at high rates of shear. There is no way in which one can measure the rate of shear produced by the finger method so it is hard to say just how high it may be. It seems that the plastometer does not furnish high enough rates of shear to make the difference in tack of the two inks apparent.

It is difficult to say what pressure would be required to give a rate of shear comparable to that produced in a lithographic ink when it is being run on an offset press. Under these conditions, a thin film of ink is transferred from the ink rollers to the plate, then to the blanket and then to the paper at a peripheral speed which averages about 120 cm. per second. It seems safe to conclude that the rate of shear obtained by extrusion plastometer is not sufficiently high to compare with this rate. It is probably for this reason that the plastometer gave no data corresponding to the tackiness of an ink.

The Study of Aging of a Hydrous Aluminum Oxide Ink.

In the previous work it was observed that when working with a hydrous aluminum oxide ink over a period of time it was impossible to get check results with the plastometer. When this particular type of ink was allowed to remain in a

container for several days, its mobility decreased. Even when run over the mill several times before testing with the plastometer the time of extrusion was longer than when the ink was first prepared. These results indicated that an aging effect was taking place in the ink and in order to determine the extent and nature of this aging effect it was decided to make a systematic study of the phenomenon.

A quantity of ink(640 gr.), sufficient for twelve runs, was made. Samples of this ink were run at regular intervals under identically the same conditions. The first sample was run through the plastometer immediately after preparation, both dry and saturated. This procedure was repeated on the 2nd, 4th, 8th, 16th, 32nd, and 64th days after preparation. Each sample of ink to be tested, after the first day, was run over the mill twice before being put in the plastometer. The sample that was run wet was treated in a similar way and then saturated with water.

The ink used in this study had the following composition:

Hydrous Aluminum Oxide -----	35 parts
------------------------------	----------

#1 Varnish -----	65 parts
------------------	----------

The pigment was first mixed into the varnish and then thoroughly ground on the ink mill. The conditions and the results obtained when the ink was run immediately after preparation, both dry and saturated with moisture, are given in Table X; Table XI contains the results obtained with the dry and saturated ink on the 8th day; Table XII, the results obtained on the 32nd day; and Table XIII the results obtained

Table X Study of Aging of Hydrous Aluminum Oxide Ink.

Run 1.

Conditions:-----

Temperature-----25 C. Pressure-----744 mm.
 Density of ink---1.190 Radius of capillary---0.2047 cm.
 % water in dry ink--5.39 Length of capillary--10.0165 cm.
 Ink run immediately after preparation in aging series.

1. Tube Reading	2. Time in Seconds	3. dt	4. dV	5. dV/dt	6. Corrected Ave. Pres.
0-5	3.8	3.8	1.744	0.459	353
10	8.8	5.0	1.835	.366	284
15	14.9	6.1	1.780	.292	232
20	22.3	7.4	1.787	.241	193
25	31.1	8.8	1.777	.202	163
30	41.9	10.8	1.736	.161	141
35	54.6	12.7	1.783	.140	121
40	72.0	17.4	1.788	.105	103
45	91.9	19.9	1.789	.092	86
50	115.2	28.3	1.795	.077	71
52	121.4	11.2	.701	.063	62
56	157.6	15.4	.700	.045	52
60	194.8	20.4	.699	.034	42
64	244.2	26.8	.699	.026	33
68	322.6	46.2	.704	.017	24
72	453	72.0	.709	.0098	17

Run 2.

Same ink as above but saturated with water. % water--33.2

0-5	4	4	1.744	0.436	353
10	9.6	5.6	1.835	.328	284
15	16.8	7.2	1.780	.248	232
20	26.6	9.8	1.787	.182	193
25	40.8	14.2	1.777	.125	163
30	59.0	18.2	1.736	.096	141
35	86.4	27.4	1.783	.065	121
40	124.8	38.4	1.788	.046	103
45	175.2	50.4	1.789	.035	86
50	248.8	73.6	1.795	.024	71
52	287.8	39.0	.701	.018	62
56	399.6	63.4	.700	.011	52
60	596.2	116.8	.699	.006	42
64	1044.6	228.2	.699	.003	33
68	1928	542	.704	.001	24
72	4380	1500	.709	.0005	17

Table XI Continuation of the Aging Test. Dry ink run
on the 8th day after Preparation.

Run 3.

Conditions same as before except:--

Pressure-----745 mm.

% water-----3.42

1. Tube Reading	2. Time in Seconds	3. dt	4. dV	5. dV/dt	6. Corrected Ave. Pres.
0-5	4	4	1.744	0.436	353
10	9.3	5.3	1.835	.348	284
15	15.8	6.5	1.780	.266	232
20	23.8	8.0	1.787	.224	193
25	34.2	10.4	1.777	.171	163
30	46.2	12	1.736	.144	141
35	60.8	14.6	1.783	.122	121
40	79.8	19	1.788	.094	103
45	103.2	23.4	1.789	.077	86
50	132.8	29.6	1.795	.061	71
52	147.6	14.8	.701	.048	62
56	180.6	16.8	.700	.042	52
60	223.8	21.4	.699	.033	42
64	282.6	32.8	.699	.021	33
68	374.8	53.2	.704	.013	24
72	565.0	115	.709	.006	17

Run 4.

Same ink as above but saturated. % water---27.3

0-5	5	5	1.744	0.351	353
10	12.2	7.2	1.835	.255	284
15	21.6	9.4	1.780	.189	232
20	44.8	13.2	1.787	.135	193
25	61.6	16.8	1.777	.106	163
30	83.6	22	1.736	.079	141
35	112.8	29.2	1.783	.061	121
40	163.2	40.4	1.788	.044	103
45	219.6	56.4	1.789	.032	86
50	301.8	82.2	1.795	.022	71
52	346.6	44.8	.701	.016	62
56	468.2	67.6	.700	.010	52
60	662.4	124.2	.699	.006	42
64	1115	280.6	.699	.003	33
68	2340	795	.704	.0009	24
72	6660	2820	.709	.0002	17

Table XII Continuation of the Aging Test. Dry ink run
on 32nd day after Preparation.

Run 5.

Conditions same as before except:--

Pressure-----746 mm.

% water-----3.93

1. Tube Reading	2. Time in Seconds	3. dt	4. dV	5. dV/dt	6. Corrected Ave. Pres.
0-5	4.8	4.8	1.744	0.364	353
10	10.7	5.9	1.835	.311	284
15	18.1	7.4	1.780	.241	232
20	27.3	9.2	1.787	.194	193
25	39.5	12.2	1.777	.146	163
30	54.2	14.7	1.736	.127	141
35	71.4	17.2	1.783	.104	121
40	95.6	24.2	1.788	.074	103
45	124.2	28.6	1.789	.063	86
50	160.6	36.4	1.795	.049	71
52	178.8	18.2	.701	.039	62
56	221.4	22.8	.700	.031	52
60	278.6	31.2	.699	.022	42
64	359.2	45.4	.699	.015	33
68	495.8	83.6	.704	.008	24
72	806	193.8	.709	.0036	17

Run 6.

Same ink as above but saturated. % water--26.52

0-5	6.3	6.3	1.744	0.276	353
10	15.4	9.1	1.835	.202	284
15	27	11.6	1.780	.153	232
20	43.4	16.4	1.787	.109	193
25	66	22.6	1.777	.0786	163
30	94.8	28.8	1.736	.0603	141
35	135.6	40.8	1.783	.0437	121
40	192.6	57	1.788	.0314	103
45	276.6	84	1.789	.0213	86
50	408.8	132.2	1.795	.0136	71
52	487	78.2	.701	.0090	62
56	720	135	.700	.0052	52
60	1172	269	.699	.0026	42
64	2145	600	.699	.0012	33
68	4520	1490	.704	.0004	24
72			.709		

Table XIII Continuation of the Aging Test. Dry ink run
on 64th day after Preparation.

Run 7.

Conditions same as before except:----

Pressure-----746 mm.

% water-----3.95

1. Tube Reading	2. Time in Seconds	3. dt	4. dV	5. dV/dt	6. Corrected Ave. Pres.
0-5	5.6	5.6	1.744	0.312	353
10	13	7.4	1.835	.242	284
15	22.5	9.5	1.780	.188	232
20	34	11.5	1.787	.155	193
25	49	15	1.777	.118	163
30	67.2	18.2	1.736	.0956	141
35	90.2	23	1.783	.0775	121
40	120.4	30.2	1.788	.0596	103
45	159.4	39	1.789	.0491	86
50	210.2	50.8	1.795	.0353	71
52	235.8	25.6	.701	.0274	62
56	300.6	35.2	.700	.0199	52
60	391.6	51.2	.699	.0136	42
64	534.2	82.4	.699	.0085	33
68	828	182	.704	.0039	24
72	2280	1090	.709	.0006	17
					13

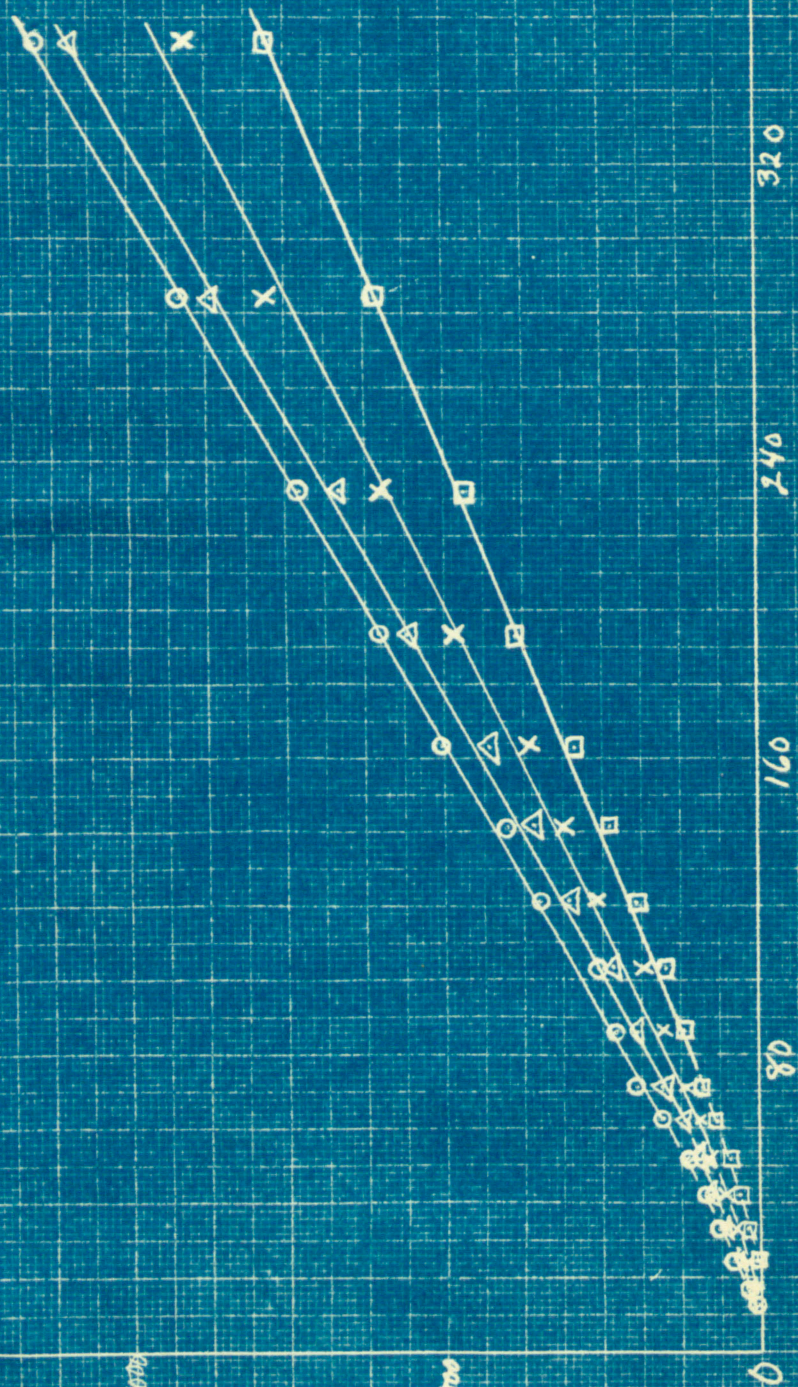
Run 8.

Same ink as above but saturated. % water--26.64

0-5	7.7	7.7	1.744	0.2264	353
10	18.6	10.9	1.835	.1686	284
15	33.2	14.6	1.780	.1220	232
20	52.6	19.4	1.787	.0921	193
25	79	26.4	1.777	.0673	163
30	113	34	1.736	.0511	141
35	157.8	44.8	1.783	.0398	121
40	226.2	68.4	1.788	.0261	103
45	323.8	97.6	1.789	.0183	86
50	480.6	156.8	1.795	.0114	71
52	571	90.5	.701	.0078	62
56	850	161.8	.700	.0043	52
60	1390	325	.699	.0022	42
64	2585	750	.699	.0009	33
68	5400	1860	.704	.0003	24

Plotted from tables I - VIII inclusively
 O Dry INK run immediately after preparation
 Δ ON 8th day
 X 32nd
 □ 64th

$\frac{dv}{dt}$ - Rate of flow in $\frac{cm^3}{sec.}$



Pressure in cm. of Hg

Figure 8.

Results Plotted from tables I & III

○ DRY INK ON 1st day after preparation.

△ Saturated INK run on same day

X DRY INK 64 days after preparation

□ Saturated INK run on same day

$\frac{dV}{dt}$ - Rate of flow in $\frac{cm^3}{sec}$

Pressure in cm. of Hg

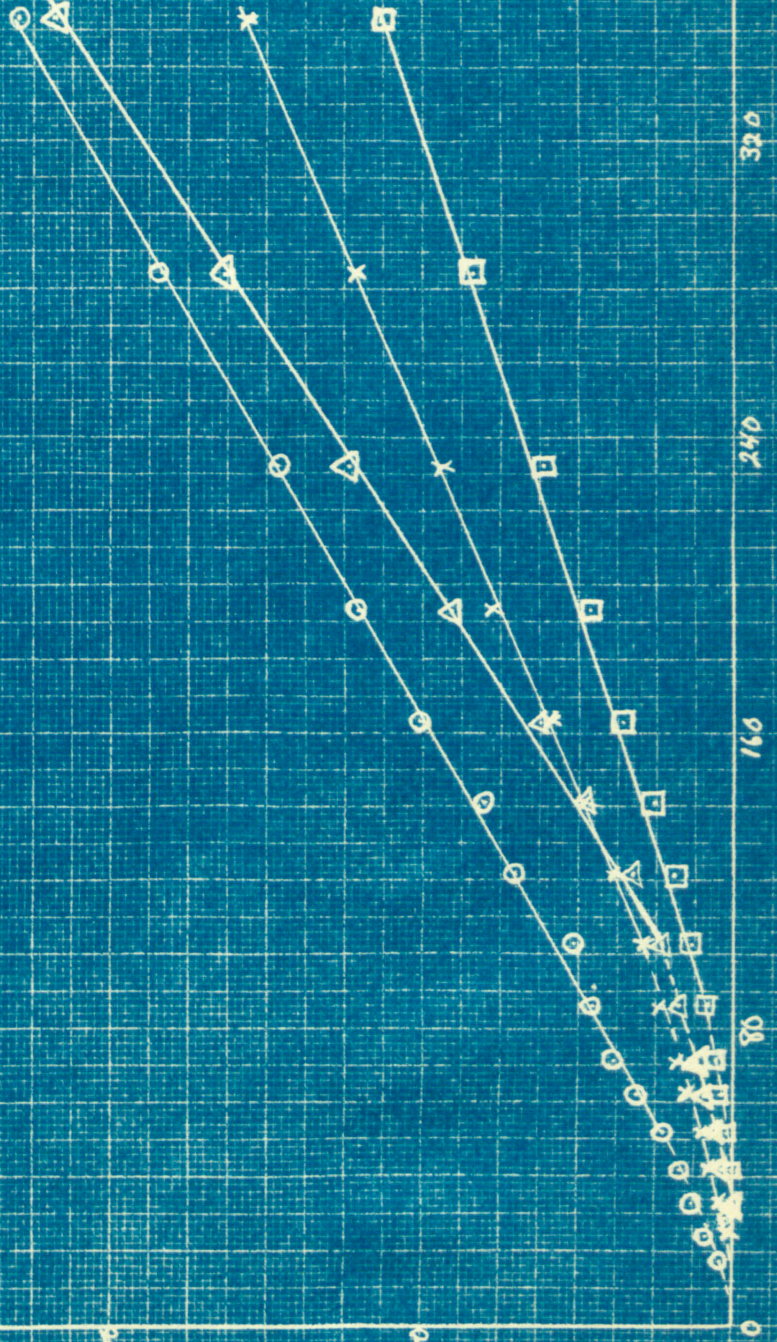


Figure 9.

Plotted from tables X - XIII inclusively

○ Saturated ink run immediately after preparation
 △ on 8th day
 x 32nd
 □ 64th

$\frac{dV}{dt}$ - Rate of flow in $\frac{cm^3}{sec}$

Pressure in cm. of Hg

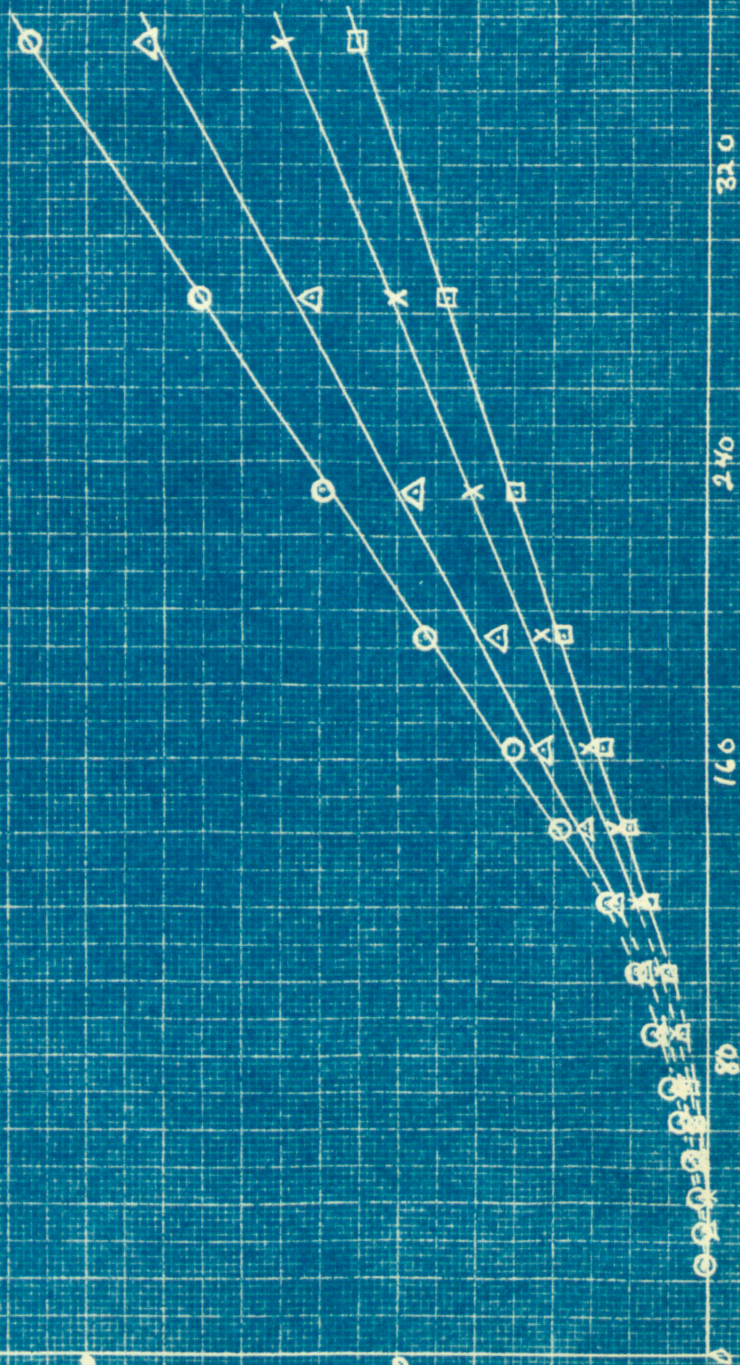


Figure 10.

on the 64th day. The results of the runs made on the 2nd, 4th, and 16th days after preparation are not included because the amounts of aging in these short intervals of time were comparatively slight. These results are shown graphically in Figure 8.

This data gives definite proof that a hydrous aluminum oxide ink becomes less mobile with aging. The slope of the curve on the 8th day is less than that of the first and that on the 32nd day is less than that of the 8th day, and so forth.

In Figure 9 the results obtained on the 1st and 64th days are compared both in the dry and saturated states. This brings out more emphatically the extent of the aging effect.

The effect of water on the consistency of the ink is shown in Figure 10. It will be noticed that the mobility and the length of the ink are considerably reduced as indicated by the decrease in the slope of the curve and an increase in yield value.

It seemed quite evident that there were two distinct types of aging taking place in the inks; the one type being reversible and the other irreversible. The carbon black ink was an example of the first type. If a sample was allowed to remain in a container over a period of several weeks it became stiff and immobile. However, if it was worked on the slab or run over the mill it would return to its original consistency. Undoubtedly, what happened

was that the inert pigment particles during the aging tended to flocculate and group together, thus making the mass rigid. This flocculation and agglomeration was broken up by the grinding and the particles were again dispersed.

The irreversible type of aging was exemplified by the hydrous aluminum oxide ink. In this case there seemed to be a definite chemical change whereby the hydrous aluminum oxide reacted with the free fatty acid of the varnish to form an aluminum soap. In this case, no amount of grinding would cause the ink to return to its original consistency. The ink was chemically altered, and hence the change in consistency was irreversible.

In connection with the study of aging of inks, it was considered advisable to determine the acid values (see Table I) of the varnishes used. The acid value of the #1 varnish was found to be 15.60 milligrams KOH.

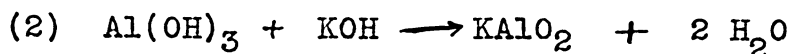
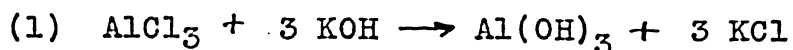
Trouble was encountered in attempting to use the usual method for acid value in determining the acid value of the mixture of varnish and hydrous aluminum oxide. Phenolphthalein was used as the indicator. It changed from colorless to red at a pH of 8. As alcoholic KOH was added to the suspension of ink, a deep red color would be produced. With $\text{Al}_2(\text{OH})_6$ present, this color would not persist for ten seconds or longer as in the case of the varnish alone, but would disappear in five or six seconds. Addition of KOH could be continued until the amount of KOH used was far in excess of that required to neutralize the free acid without reaching a satisfactory endpoint.

This was explained by the fact that a chemical reaction took place between the KOH and the hydrous aluminum oxide to form potassium meta aluminate as was established by the work of Hildebrand and Blum (25),

(25) Mellor, J. W., "Comprehensive Treatise on Inorganic and Theoretical Chemistry" (1924) Vol. V., p. 288.

They found that by starting with an aluminum salt and adding KOH, a precipitate of $\text{Al}(\text{OH})_3$ starts to form at a pH of 3.0. The precipitation stopped at a pH of 7, with the dissolution of the $\text{Al}(\text{OH})_3$ in excess KOH to form KAlO_2 .

The reactions were as follows:



Reaction (1) starts when a pH of 3 is reached and the precipitation continues until a pH of 7 is attained, above which reaction (2) takes place. Thus reaction (2) explains why so much KOH was required when the attempt was made to titrate the free fatty acid of the varnish in the ink.

The next logical thing to try was the removal of the pigment before attempting the titration. A centrifuge was not available for this purpose. It was observed, however, that a complete dispersion of both the varnish and the pigment was obtained when ether alone was used as the solvent. Then by the addition of the optimum amount of alcohol (determined experimentally) the hydrous aluminum oxide was caused to flocculate and settle.

Thus a four-gram sample of ink was weighed and dissolved with 77.6 c.c. of neutral ether and 26.4 c.c. of 95% alcohol was then added and the sample was allowed to settle for one hour. Three aliquot parts of 25 c.c. each were then pipetted out and titrated. By the use of this method, the acid value of the varnish, after it had been in contact with the hydrous aluminum oxide for four weeks, was found to be 10.40 milligrams KOH, indicating that 5.19 milligrams of the free fatty acid had disappeared and confirming the belief that part of it had been used up in soap formation.

In the previous work with the hydrous aluminum oxide ink, it was observed that the aging took place very much more rapidly when the ink was saturated with water. The ink, immediately after being saturated, was found to be less mobile and shorter than the dry ink as shown in Figure 8. It was observed that as the saturated ink was allowed to age for a longer time its mobility rapidly decreased to the point where it was practically solid.

This is illustrated by the work done on the 32nd day and following. The ink was run on the plastometer both dry and saturated with water. The results are given in Table XII. The saturated ink was then placed in a can and covered over with water to prevent oxidation by the air. Two days later the excess water was removed, the saturated ink worked on the slab and then run through the plastometer

under conditions identical with previous runs. The results are given in the following table, Table XIV.

Table XIV Plastometer Data on Sample of Ink after being Saturated with Water for 48 Hours.

Conditions:--Same as in Table XIII.

1. Tube Reading	2. Time in Seconds	3. dt	4. dV	5. dV/dt	6. Corrected Ave. Pres.
0-5	225	225	1.744	0.0078	353
10	715	490	1.835	.0037	284
15	1461	746	1.780	.0024	232
20	2852	1391	1.787	.0013	193

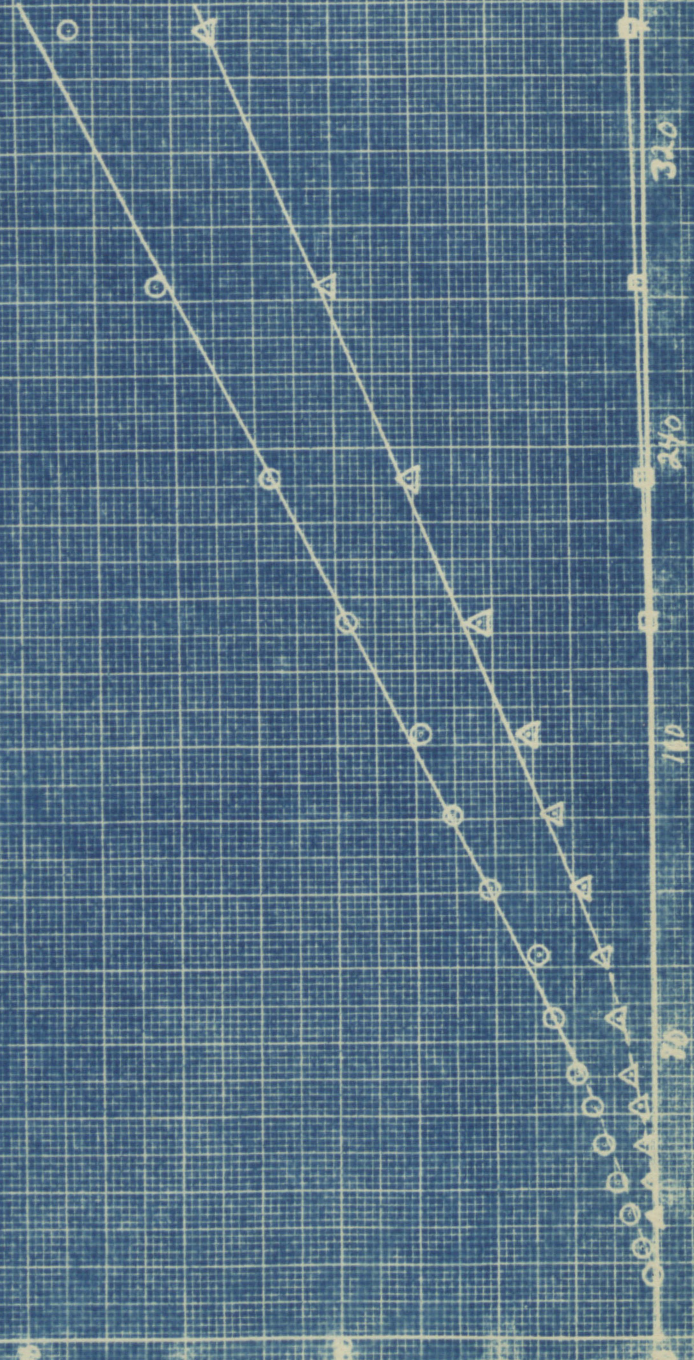
On the fourth day after the ink was saturated, an attempt was made to run it through the plastometer. This was found impossible because the ink had developed so much rigidity that it could not be put into the plastic reservoir, let alone forced through the capillary.

The results of these tests are shown graphically in Figure 11, which embodies the plotted data from Tables XII and XIV, and shows that the soap formation in the ink is strongly catalyzed by the presence of water. The reaction whereby the soap formation occurs is very slow in the case of the dry ink, but is speeded up to a marked degree by the presence of water.

Results Plotted from tables XII & XIV

- DRY INK run on 32nd day
- △ Saturated INK run on same day
- ~~4 days later~~ 4 days later, still not in run
- x

Rate of flow in cm³/sec



Pressure in cm. of Hg

Figure 11.

It is quite common for ink which contains hydrous aluminum oxide to "liver". The trouble very likely is that the pigment used contains a relatively large amount of water, perhaps $\text{Al}_2\text{O}_3 \cdot 8 \text{H}_2\text{O}$ or even more. The presence of excess water may then be the cause of "livering". The difficulties that the ink maker experiences with aluminum hydrate, are, however, only incidental to this study, but deserve further research.

Another sample of the saturated ink containing 26.49% water was taken twenty-four hours after being saturated. This was run over the mill for one hour to remove the water by evaporation, and at the same time to bring it back as nearly as possible to its original consistency. At the end of one hour, the water content was found by analysis to have been reduced to 4.22%. However, the ink itself had not been reduced to anything like its original consistency. The dry ink in the beginning was amber colored, about the color of honey. Upon working water into the ink, it became white and opaque. Upon removing the water by evaporation, the ink changed to a dark gray color, it became less mobile and the length remained about the same. There was a great increase in tack. Thus the elimination of water from the aged, saturated hydrous aluminum oxide ink failed to restore the original consistency of the ink. This irreversibility is additional proof that a chemical reaction takes place between the pigment and the vehicle.

A Study of the Effects of Variation of Concentration in
Pigment and Vehicle.

Further work was concerned with the preparation and the study of a series of inks in which the proportions of pigment and vehicle were varied. It was hoped by such a study that certain properties of the plastics could be ascribed to the pigment and others to the vehicle.

In this work, four series of inks were prepared, each series being composed of five inks. Hydrous aluminum oxide was the only pigment used. Four varnishes having different physical and chemical properties (see Table I) were employed.

The following is the list of formulas of the inks prepared and studied.

Series I

	Ink No. 1.	2.	3.	4.	5.
#0000 varnish -----	50	47.5	45	42.5	40
Hydrous aluminum oxide --	50	52.5	55	57.5	60

Series II

#00 varnish -----	57.5	55	52.5	50	47.5
Hydrous aluminum oxide --	42.5	55	57.5	50	52.5

Series III

#1 varnish -----	67.5	65	62.5	60	57.5
Hydrous aluminum oxide --	32.5	35	37.5	40	42.5

Series IV

#0000 varnish -----	51.8	49.5	47.3	45	42.8
#7 varnish -----	5.7	5.5	5.2	5	4.7
Hydrous aluminum oxide --	42.5	45.0	47.5	50	52.5

In working out the above formulae it was the aim to cover the whole range of consistencies of lithographic inks. The inks with the low concentration of pigment were more mobile and thinner than the intermediate inks which had approximately the same consistency as used on the press. Thus the inks with the high concentration of pigment were much less mobile than those used on the press. The concentrated inks are comparable to such inks as are made to be used by a pressman who insists upon having an ink that requires reducing or doctoring.

The four series of inks were tested by means of the extrusion plastometer directly after preparation. (They were later tested using an instrument which it was hoped would give information concerning tack.) A description of design, construction, and use of this instrument will be given later when a comparison will be made with the plasmetric results. The discussion here will be concerned with the study made with the plastometer.)

It is a well-known fact that by the use of Poiseuille's equation one can calculate the absolute viscosity of a liquid. Thus:

$$N = K' \frac{P}{V} \quad (1)$$

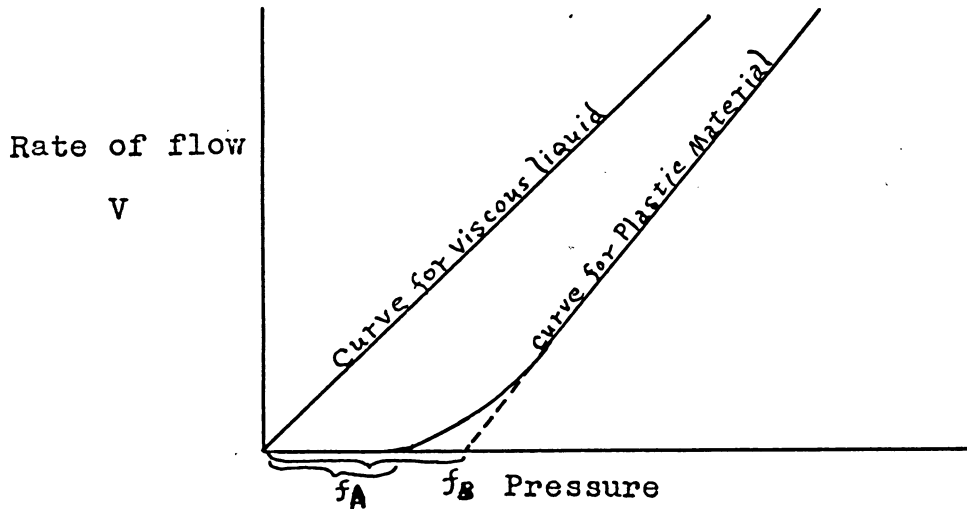
where N-----absolute viscosity

K'-----capillary constant and depends upon the dimension of the capillary, i.e. $K' = \frac{\pi r^4 g}{8 l}$

P-----pressure causing flow

V-----volume of flow/second

By plotting rate of flow against pressure for a viscous liquid you get the following result:



It follows from the linear character of the curve passing through the origin that the viscous flow is directly proportional to the pressure, in other words $\frac{P}{V}$ is a constant. However, in the case of a plastic material, the slope of the curve is accurately defined by $\frac{P - f}{V}$, where f is the intercept on the pressure axis; thus we have

$$R = K' \frac{P - f}{V} \quad (2)$$

where R , the rigidity of a plastic, is comparable to N , the viscosity of a liquid.

The analogy can be carried still further by the fact that the reciprocal of viscosity is fluidity, that is, $\frac{1}{N} = \phi$; then the reciprocal of rigidity is mobility, that is, $\frac{1}{R} = \mu$.

$$\therefore \mu = K \frac{V}{P - f} \quad (3)$$

where K = capillary constant = $\frac{8 l}{\pi r^4 g}$

V = volume of flow/second

P = total pressure expressed in grams/sq. cm.

f = yield value, i.e., pressure below which no flow takes place and above which it does take place.

This equation was used in calculating the mobility of the inks in the various series. This was done by first calculating the constant K , of the capillary used in the study of the entire series of inks. An etched capillary having a length of 10.0456 cm. and a radius of 0.2077 was used. Therefore,

$$K = \frac{8 l}{\pi r^4 g} = \frac{8 \times 10.0456}{3.1416 \times 0.2077 \times 980}$$

$$K = 17.658$$

The values V , P , and f , which are the variables in equation (3) were obtained from the experimental results given in Table XV. The value V , for example, is the volume extruded, divided by the time in seconds. The pressure P , in centimeters of mercury which has been used so far, was converted into grams/square cm. This is accomplished by multiplying the centimeters of mercury by 13.54 grams, (density of mercury at 25 C.). This was necessary on account of the fact that the mobility is to be expressed in C. G. S. units.

In these calculations two methods were used in arriving at the value to be used as the yield point, f , (the point

of intersection with the pressure axis). The first method was that of determining the pressure at which the flow through the capillary actually stopped. This point will be found designated f_A in Table XV. The second method was by extending the straight part of the pressure-rate of flow curve to the pressure axis. This is the method used by Bingham (26),

(26) Bingham and Green, - American Society for Testing Materials, 18, Part II, p. 643 (1919).

and this yield point will be designated by f_B in Table XV. Consequently the use of two values of f gave two values of mobility (μ) as a result of employing equation (3). The mobility calculated by the use of the value f_A was labeled μ_A , and of f_B as μ_B .

In Table XV, series I, ink #1 for the first reading, the following data were obtained:

$$P = 2071.6 \text{ gms./sq. cm.}$$

$$V = 0.750$$

$$f_A = 3.27 \text{ gms./sq. cm.}$$

The calculated value of $K = 17.658$

$$\therefore \mu = K \frac{V}{P - f_A} = 17.658 \frac{0.750}{2071.6 - 3.27}$$

$$\mu_A = 0.00641 \text{ poises}$$

In an analogous manner, the mobility was calculated for the other readings. It will be noticed (Table XV) that the values of μ_A are not constant. This value is smaller also than the value of μ_B .

Table XV. Series I.

A Study of Variation in Concentration in Pigment and Vehicle.

Conditions under which Ink 1 was run:--

Temperature-----25 C.

Pressure-----748 mm.

Length of capillary-----10.0456 cm.

Radius of capillary-----0.2077 cm.
Density of ink-----1.300

Ink 1.

1. Pressure in cm Hg.	2. Pressure gm/sq.cm.	3. dt	4. dv	5. $\frac{dv}{dt}$	6. f_A gm/sq.cm.	7. μ_A	8. f_B gm/sq.cm.	9. μ_B
153	2071.6	4.7	3.513	0.750	3.3	0.00641	75	0.00662
110.6	1497.5	6.8	3.601	.535		.00632		
78.2	1058.8	10.2	3.584	.352		.00590		
52.3	708.1	15.0	3.502	.234		.00586		
29.8	403.4	31	3.634	.117		.00515		
8.4	113.7	211	3.454	.016		.00257		

Ink 2. - Density--1.350.

152.8	2068.8	7	3.513	0.501	8.25	0.00429	160	0.00474
110.4	1494.8	10	3.601	.360		.00428		
77.8	1053.4	15	3.584	.239		.00404		
51.8	701.4	24	3.502	.146		.00372		
29.2	395.4	57	3.634	.064		.00292		
7.8	105.6	775	3.454	.0044		.00091		

Ink 3. - Density--1.368.

213.5	2890.8	7	3.567	0.510	98.6	0.00322	640	0.00400
152.2	2060.9	11.6	3.513	.332		.00299		
110.3	1493.4	18.6	3.601	.194		.00246		
77.8	1053.4	31.2	3.584	.115		.00213		
51.8	701.4	57.4	3.502	.061		.00179		
29.2	395.4	178.4	3.634	.0204		.00121		
12.2	165.2	1490	3.454	.0016		.00042		

Table XV. Continued.

Ink 4. - Density--1.380.

1. Pressure in cm. Hg.	2. Pressure gm./sq. cm.	3. dt	4. dv	5. $\frac{dv}{dt}$ v	6. f_A gm./sq. cm.	7. μ_A	8. f_B gm./sq. cm.	9. μ_B
318.8	4316.6	6.8	3.579	0.525	161.6	0.00223	820	0.00265
213.4	2890.8	12.2	3.567	.292		.00189		
152.2	2060.9	19	3.513	.185		.00172		
110.2	1493.4	34	3.601	.106		.00141		
77.8	1053.4	64	3.584	.056		.00111		
51.8	701.4	147	3.502	.024		.00078		
29.2	395.4	857	3.634	.0042		.00032		

Ink 5. - Density--1.450

319.6	4327.5	22	3.579	0.163	1200	0.00092	1440	0.00099
213.6	2892	43.6	3.567	.082		.00086		
151.5	2051	92.4	3.513	.038		.00079		
108	1462	287	3.601	.0013		.00008		

Table XVI. Series II.

A Continuation of Study in Variation in Concentration.

Conditions under which this series of inks were run: Length of capillary---10.0456 cm.
 Temperature-----25 C. Radius of capillary-----0.2077 cm.
 Pressure-----747 mm.

Ink 1. - Density--1.260.

1. Pressure, gm./sq. cm. Hg.	2. dt	3. dv	4. $\frac{dv}{dt}$ v	5. f _A	6. μ_A	7. f _B	8. μ_B
2890	4.6	3.567	0.775	6.8	0.00474	150	0.00499
1940.8	7	3.513	.502				
1495	9.6	3.601	.375				
1053.4	14.2	3.584	.251				
701.6	23.8	3.502	.160				
395.4	47.4	3.634	.077				
180.9	60	1.727	.029				
105.6	371	3.454	.009				

Ink 2. - Density--1.270.

1.	2.	3.	4.	5.	6.	7.	8.
4318	4.2	3.579	0.852	14.92	0.00348	540	0.00400
2889.8	6.8	3.567	.525				
1940	11	3.513	.320				
1497.7	15.8	3.601	.228				
1053	24	3.584	.149				
701.3	92	3.502	.086				
395.2	42	3.634	.040				
220.1	58	.7181	.017				
169.4	100	.7181	.012				
105.6		.7145	.007				

Table XVI. Continued.

Ink 3. - Density--1.290. - Pressure--745 mm.							
1. Pressure gm./sq.cm. Hg.	2. dt	3. dv	4. $v = \frac{dv}{dt}$	5. f _A	6. μ_A	7. f _B	8. μ_B
4317.8	6.8	3.579	0.525	130	0.00222	700	0.00256
2889.7	11.4	3.567	.314				
2062.2	18.0	3.513	.195				
1494.7	29.8	3.601	.121				
1052.8	50.6	3.584	.071				
701.0	101.4	3.502	.035				
394.8	282	3.630	.0095				
219.8	300	.7181	.0024				
169.4	750	.7181	.0009				
Ink 4. - Density--1.315. - Pressure--743 mm.							
4317.6	11.4	3.579	0.314	289.4	0.00137	800	0.00160
2889.5	18.6	3.567	.192				
2062	32	3.513	.110				
1494.5	57.6	3.601	.063				
1052.6	120.4	3.584	.030				
701	337	3.502	.010				
501	155	.7005	.0045				
433	230	.7005	.0030				
378.9	420	.7048	.0017				
311	900	.7048	.0008				
Ink 5. - Density 1.330.							
4778.2	14	1.744	0.125	1600	0.00070	1760	0.00073
3884	20.2	1.835	.091				
3140	30.8	1.780	.058				
2612	48	1.787	.037				
2205	79	1.777	.022				
1908	216	1.736	.008				

Table XVII. Series III.

A Continuation of Study in Variation in Concentration.

Conditions under which this series of inks were run:
 Temperature-----25 C. Same capillary.
 Pressure-----739 mm.

Ink 1. - Density--1.1813.

1. Pressure gm./sq.cm.Hg.	2. dt	3. dv	4. $\frac{dv}{v} = \frac{dt}{dt}$	5. f _A	6. μ_A	7. f _B	8. μ_B
4331	5	3.579	0.715	5.42	0.00292	320	0.00315
2907	7.8	3.567	.457				
2078.5	11.6	3.513	.308				
1520.5	16.8	3.601	.215				
1064	25.8	3.584	.139				
734	38	3.502	.0925				
406	75	3.634	.0485				
237	30	.7181	.0240				
183	38	.7181	.0189				
113.7	52	.7145	.0138				
74.5	95	.6840	.0072				

Ink 2. - Density--1.1915.

Pressure--750 mm.

4315	6.8	3.579	0.525	40.62	0.00216	470	0.00240
2891	11.2	3.567	.319				
2063.5	17	3.513	.206				
1492	25	3.601	.144				
1051	37	3.584	.097				
719	61	3.502	.0575				
391	140	3.634	.0260				
222.5	62	.7181	.0116				
168	90	.7181	.0080				
105.6	165	.7148	.0043				
68	585	.6840	.0012				

Table XVII. Continued.

Ink 3. - Density--1.2160. - Pressure--742 mm.

Pressure gm./sq.cm.Hg.	dt	dV	$V = \frac{dV}{dT}$	f_A	μ_A	f_B	μ_B
4327	9.4	3.579	0.381	116.4	0.00160	610	0.00176
2902	16.4	3.567	.218				
2074.5	24.2	3.513	.145				
1503	38	3.601	.095				
1060	59	3.504	.061				
730	103	3.502	.034				
402	270	3.634	.0134				
233	145	.7181	.0050				
178.7	245	.7181	.0029				
116.5	665	.7145	.0011				

Ink 4. - Density--1.237. - Pressure--740 mm.

4330	14.4	3.579	0.250	264.3	0.00108	980	0.00132
2905.7	26.8	3.567	.133				
2077	42.8	3.513	.082				
1506	73	3.601	.0495				
1063	135	3.584	.0266				
731	308	3.502	.0114				
478	600	1.754	.0030				
405	600	.7048	.0017				

Ink 5. - Density--1.260. - Pressure--736 mm.

4790.4	15	1.744	0.1165	922	0.00053	1160	0.00057
3856	20	1.835	.0915				
3152	28	1.780	.0635				
2624	39	1.787	.0457				
2218	56	1.777	.0318				
1920	79	1.736	.0220				
1650	125	1.783	.0142				
1406	223	1.818	.0082				
1175	580	1.789	.0031				

Table XVIII. Series IV.

A Continuation of Study in Variation in Concentration.

Conditions under which this series of inks were run:
 Temperature-----25 C.
 Same capillary.

Ink 1. - Density--1.241. - Pressure--748 mm.

Pressure gm./sq.cm.Hg.	dt	dV	$V = \frac{dV}{dt}$	f_A	μ_A	f_B	μ_B
4293.6	4.6	3.579	0.778	762.2	0.00389	1080	0.00427
2866	8.2	3.567	.435		.00357		
2032	15.6	3.513	.225				
1454	38.2	3.601	.095				
1005.7	189.4	3.584	.019				
785.9	239	.7014	.0029				

Ink 2. - Density--1.252. - Pressure--746 mm.

Pressure gm./sq.cm.Hg.	dt	dV	$V = \frac{dV}{dt}$	f_A	μ_A	f_B	μ_B
4294.8	5.8	3.579	0.617	802	0.00312	1460	0.00393
2868	11.4	3.567	.315		.00269		
2034	24	3.513	.146				
1455.5	64	3.601	.056				
1115.7	90.2	1.789	.020				
932.6	344	1.795	.0052				

Ink 3. - Density--1.271.

Pressure gm./sq.cm.Hg.	dt	dV	$V = \frac{dV}{dt}$	f_A	μ_A	f_B	μ_B
4296	9.8	3.579	0.365	1133	0.00204	1540	0.00234
2868	20.6	3.567	.173				
2035	53.4	3.513	.066				
1593.4	67.2	1.783	.026				
1348.3	179	1.818	.010				

Table XVIII. Continued.

Ink 4. - Density--1.285. - Pressure--745 mm.

Pressure gm./sq.cm.Hg.	dt	dV	$V = \frac{dV}{dt}$	f_A	μ_A	f_B	μ_B
4754	7.4	1.744	0.236	1590	0.00132	1930	0.00147
3817	11.8	1.835	.156				
3111.5	18.2	1.780	.098				
2579	34.2	1.787	.052				
2166.4	75.8	1.777	.023				
1864.5	201.0	1.736	.0086				

Ink 5. - Density--1.309.

4754	13	1.744	0.134	1806	0.00080	2200	0.00092
3815.6	22	1.835	.083				
3107.5	41	1.780	.043				
2575	86	1.787	.021				
2165	238	1.777	.0075				

Ink 1'.--An ink made over the same formula as #1, and run under the same conditions as the one above. - Pressure--740 mm.

4300	4.6	3.579	0.778	704	0.00382	1020	0.00420
2873	8.2	3.567	.435				
2044.6	15	3.513	.234				
1468	32.2	3.601	.112				
1021	124	3.584	.0289				
796	86	.7017	.0082				

INK #1 { 50g. alcohol
 50g. #0000 warm.
 #2 { 59.5 g. alcohol
 47.5 #0000 warm.
 #3 { 55.9 g. alcohol
 45.0 #0000 warm.
 #4 { 57.5 g. alcohol
 42.5 #0000 warm.
 #5 { 60.0 g. alcohol
 40.0 #0000 warm.

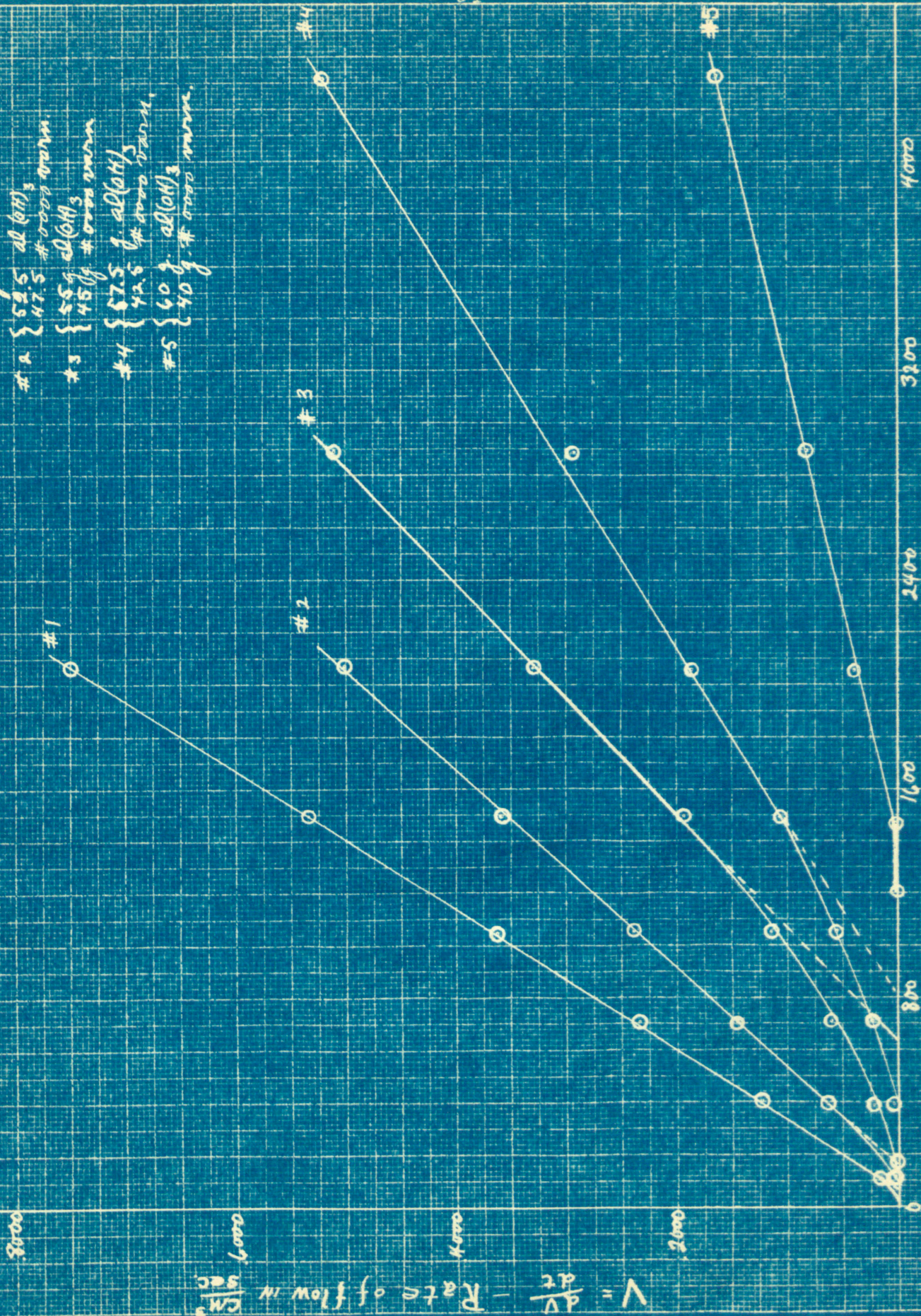
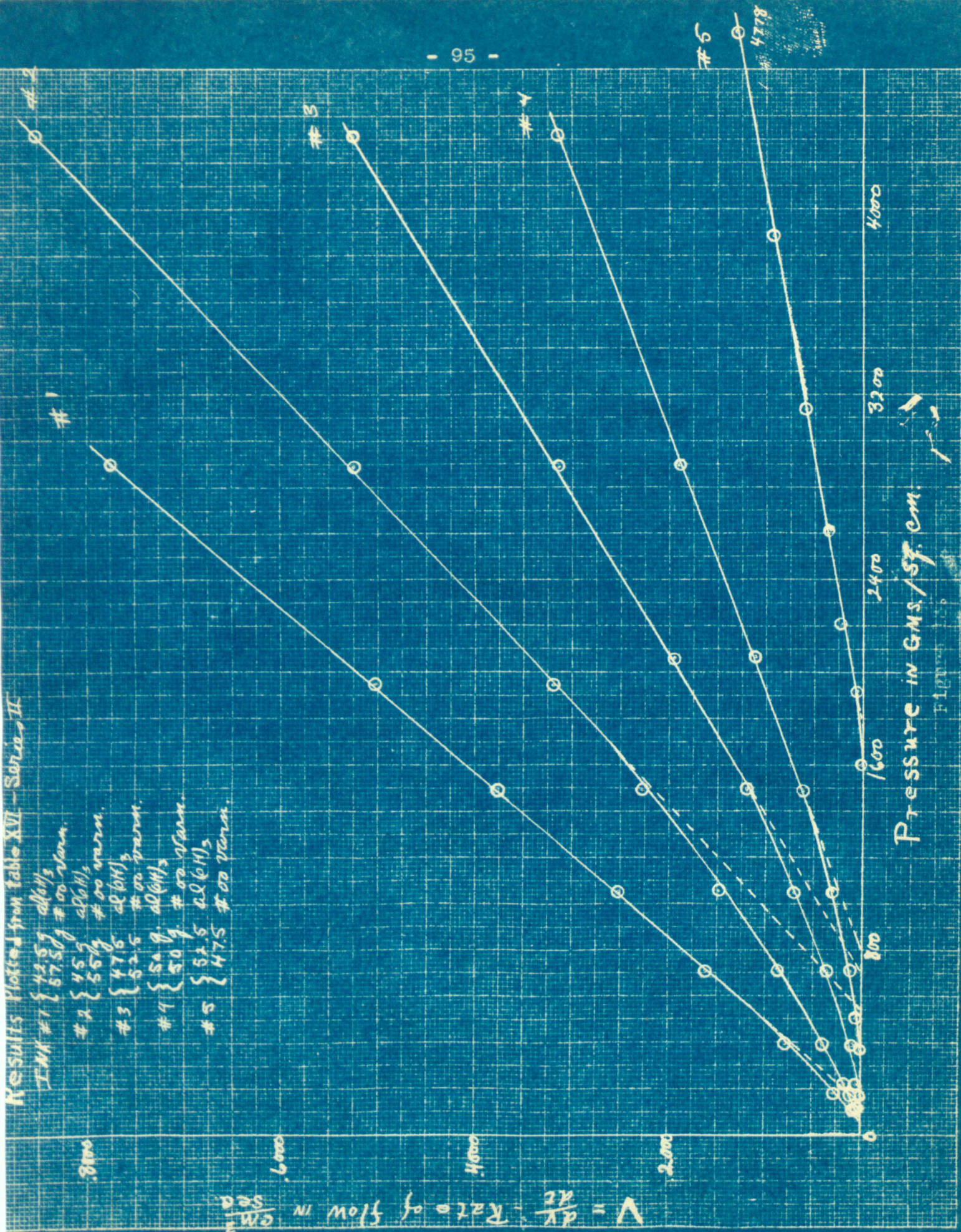


Figure 12.

Results Plotted from Table VII - Series II

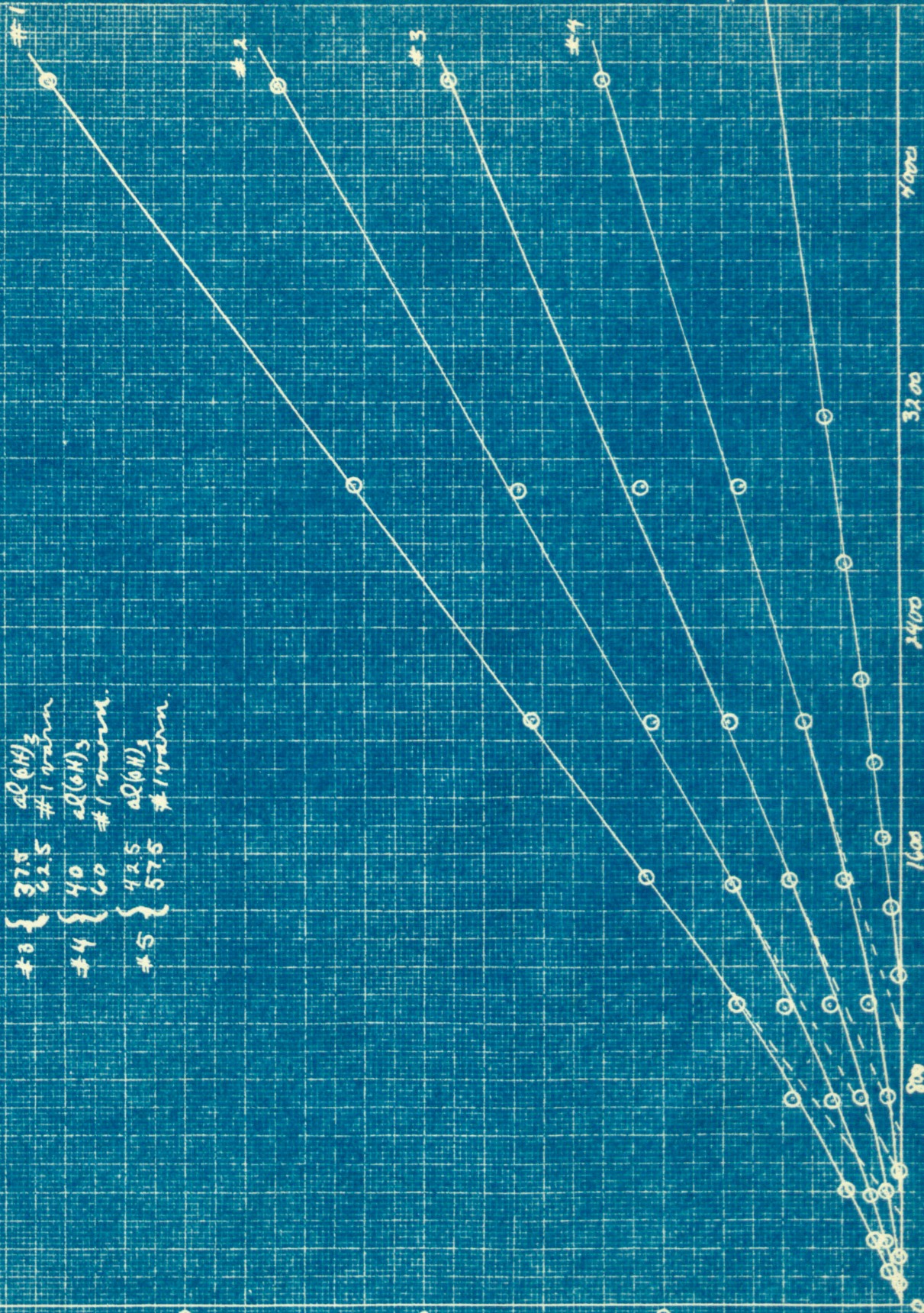
T.M. #1 { 42.5 g. $\text{Al}(\text{OH})_3$
 { 57.5 g. #00 warm.
 #2 { 45 g. $\text{Al}(\text{OH})_3$
 { 55 g. #00 warm.
 #3 { 47.5 g. $\text{Al}(\text{OH})_3$
 { 52.5 g. #00 warm.
 #4 { 50 g. $\text{Al}(\text{OH})_3$
 { 50 g. #00 warm.
 #5 { 52.5 g. $\text{Al}(\text{OH})_3$
 { 47.5 g. #00 warm.



Results Plotted from table XVII - Series III

INK #1 { 32.5g al(6H)₃
 { 67.5g #1 varn.
 #2 { 25 al(6H)₃
 { 65 #1 varn.
 #3 { 37.5 al(6H)₃
 { 62.5 #1 varn.
 #4 { 40 al(6H)₃
 { 60 #1 varn.
 #5 { 42.5 al(6H)₃
 { 57.5 #1 varn.

$V = \frac{dV}{dt} = \text{Rate of flow in } \frac{\text{cm}^3}{\text{sec.}}$
 8000
 6000
 4000
 2000



Pressure in gms./sq. cm.

Figure 14.

Results Plotted from table XVIII - Series IV

INK #1 { 42.5 g. al(6H)₃
 { 51.8 g. #0000 varn.
 { 8.7 g. #7 varn.

 #2 { 45 g. al(6H)₃
 { 49.5 g. #0000 varn.
 { 5.5 g. #7 varn.

 #3 { 47.5 g. al(6H)₃
 { 47.3 g. #0000 varn.
 { 5.2 g. #7 varn.

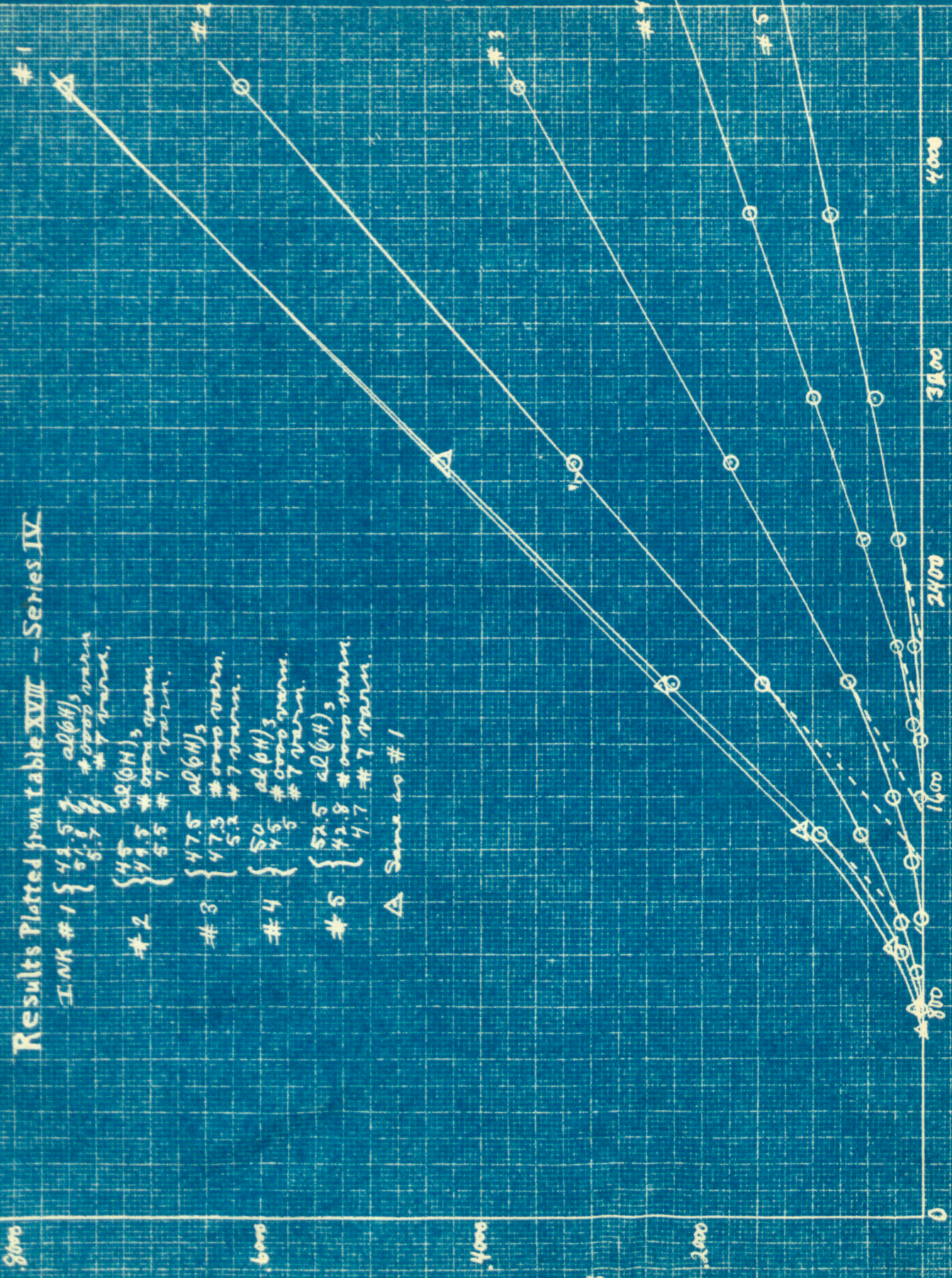
 #4 { 50 g. al(6H)₃
 { 45 g. #0000 varn.
 { 5 g. #7 varn.

 #5 { 52.5 g. al(6H)₃
 { 42.8 g. #0000 varn.
 { 4.7 g. #7 varn.

A Same as #1

$V = \frac{dV}{dt}$ - Rate of flow in $\frac{cm^3}{sec}$

Pressure in $\frac{gms}{sq. cm}$



#1 - Series I

INKS of same weight composition,
but using vehicles of different viscosities

INK #1 - Series I

50g al(6H)₃

50g #0000 varn; $\eta = 4.14$ Poises

INK #4 - Series II

50g al(6H)₃

50g #00 varn; $\eta = 14.12$

INK #4 - Series IV

50g al(6H)₃

45g #0000 varn; $\eta = 4.94$

5g #7 ; $\eta = 1460.5$

#4 - S II

#4 - S II

4754

4000

3200

2400

1600

800

Pressure in Gms./sq. cm.

Figure 16.

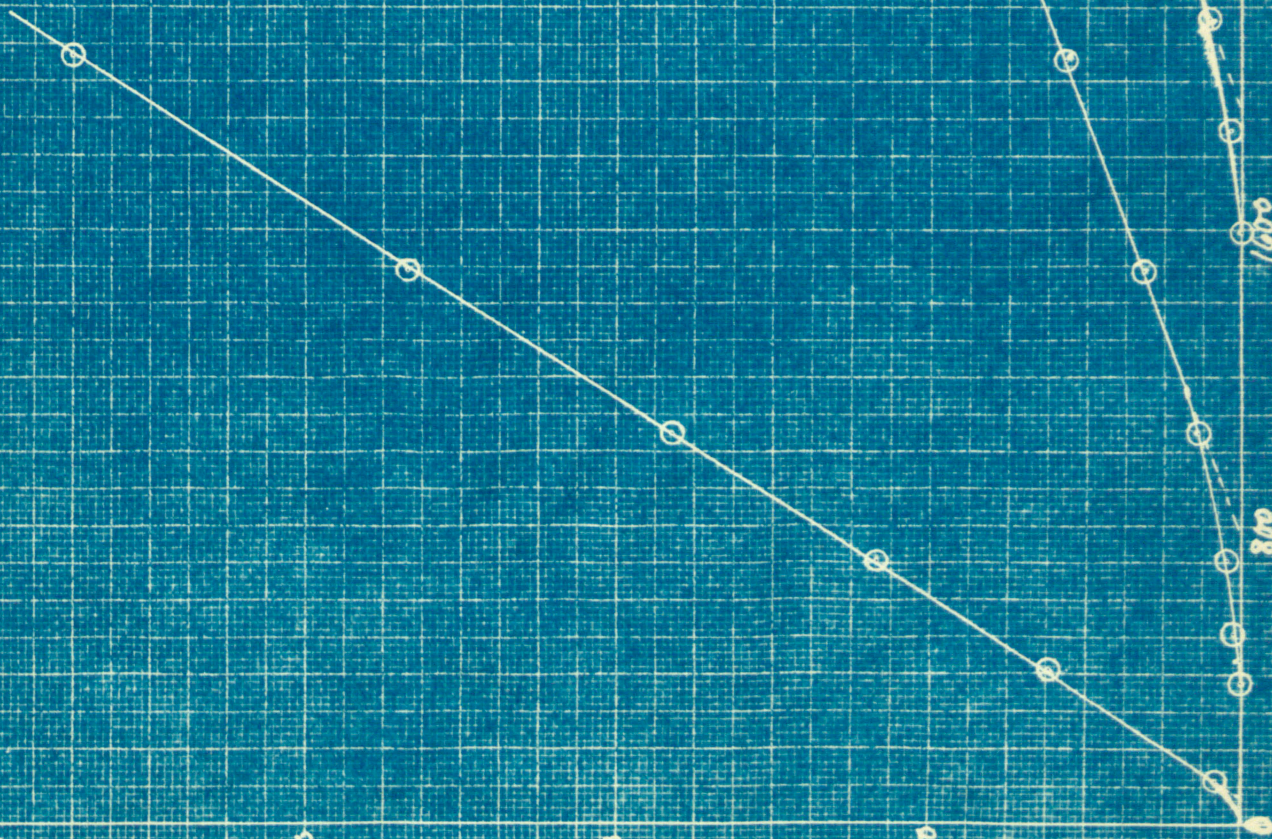
8000

6000

4000

2000

$V = \frac{dV}{dt}$ - Rate of flow in $\frac{cm^3}{sec}$



The calculation of mobility in which the value f_B is used was as follows:

$$\mu_B = 17.658 \frac{0.751}{2071.6 - 75}$$
$$\therefore \mu_B = 0.00662 \text{ poises}$$

The calculations of the mobility for the other points were carried out in a similar way. It can be seen from Table XV that the values of μ_B thus obtained are practically constant.

The results given in Tables XV, XVI, XVII, and XVIII are plotted in Figures XII, XIII, XIV, and XV respectively.

It will be observed that as the concentration of the pigment is increased, the mobilities of the respective inks are decreased and their yield values increased. The tack of the various inks increased with an increase in concentration of pigment. It will also be observed that the concentration of the pigment required to produce an ink of a given mobility varies inversely with the viscosity of the vehicle. This variation of mobility with the type of vehicle used is shown graphically in Figure 16.

Due to the fact that the yield point of a plastic is such a variable factor, its usefulness is questionable. This work shows that yield values vary with time, with concentration of pigment, with the viscosity of the vehicle, and whether it is determined with increasing or decreasing pressure.

Experimental Consideration of Yield Value

An ink made on the ink formula S-IV - #1 was prepared and run through the closed tube plastometer. The first and second readings checked the results of the previous ink of the same composition. The other readings were slightly different and the yield point was a little lower. The yield value determined in this way was found to be 704 gm./sq. cm.

A sample of the same ink was placed in the open tube plastometer. All conditions were identical to those in the experiment with the closed tube plastometer except that in this case gradually increasing pressure was applied. The starting pressure was 366 gm./sq. cm. This pressure was increased in steps of 67.7 gm./sq. cm. (5 cm. of mercury) until the yield value of the ink was reached. At a pressure of 704 gm./sq. cm. the amount of flow was very small; the amount extruded in two minutes being just enough to indicate a slight difference in the amount of ink on the end of the capillary. Flow did not continue.

Another 67.7 gm./sq. cm. increase (total pressure 771.7) made no appreciable difference in the amount extruded in the two minute interval. Another increase (total pressure 839.4 gm./sq. cm.) caused only a slight movement of the ink. The pressure was increased to 907 gm./sq. cm., then to 974.7 with only a slight change. At this pressure a plug of ink about 3 mm. long was extruded in a two minute interval.

Another 67.7 gm./sq. cm. increase (total pressure 1042 gm./sq. cm.) indicated that the yield point was just

slightly exceeded. The amount of flow the first minute was 2 mm., at the end of the second minute a plug of ink 3.2 cm. long was extruded, and at the end of the third minute, 5 cm. of the material had been extruded. Thus the yield point determined by gradually increasing the pressure was in the neighborhood of 1042 grams per square centimeter.

These results are shown graphically in Figure 16. The straight part of the curve which is extended to the pressure axis gives the yield value as determined by Bingham. This is found to be 925 gm./sq. cm.

Additional experiments were made with the same ink in the open tube plastometer. The mercury was pumped to the 1107 gm./sq. cm. mark and flow started at this high pressure. After the flow had started, the pressure was dropped to 704 gm./sq. cm. During the first minute, a 3 cm. length of ink, at the end of the second minute, a 3 cm. length of ink, at the end of the third minute a 1.7 cm. length of ink was extruded. This indicated that after flow is once started it will continue at a lower pressure than that of the static yield value.

The mercury was again pumped to the 1107 gm./sq. cm. mark and flow started. The pressure was then dropped to the 406.4 gm./sq. cm. mark. A piece of ink 3 mm. long at the end of the first minute, and a piece 1 mm. long at the end of the second minute was extruded.

This work gives proof that yield value is very indefinite and variable.

Graphical Representation of difference in Static and dynamic yield points.

① INK #1 Series IV - Dynamic Method.

Starting with high, and gradually diminishing pressure.

→ Same INK - Static Method.

Starting with low, and gradually increasing pressure.

By Dynamic Method $\begin{cases} f_A = 704 \text{ Gms./sq. cm.} \\ f_B = 925 \end{cases}$

By Static Method - $f = 1042$

$V = \frac{dv}{dt}$ - Rate of flow in $\frac{\text{cm}^3}{\text{sec}}$



Pressure in Gms./sq. cm

Experimental - Part III

Testing of Lithographic Inks with a Tackometer - A Form of a Dynamometer.

The investigation and testing of inks by means of the plastometer had failed to give any information concerning tack. The data on yield value and mobility, while being of importance in connection with body and length did not seem to tell the whole story about the consistency of an ink.

Therefore it was felt advisable to construct an instrument whereby an ink could be tested in a manner comparable to the conditions under which it is run on the press.

On an offset lithographic press the ink is placed in the fountain, whence it passes down over a series of rollers to the plate. The film of ink received by the design is then transferred to the blanket, and thence to the paper. The peripheral speed of the rollers and cylinders varies in practice from 95 to 145 centimeters per second.

In designing this instrument it was considered desirable to measure the rate of doing work on a sample of ink placed on a set of rollers driven at various rates of speed, the speed range being chosen so that conditions existing in actual practice would be duplicated. It was the aim to make all tests under conditions as nearly identical with press conditions as possible.

An instrument (see Figure 18) was constructed which was composed of two steel rollers mounted in ball bearings having a minimum of friction. The rollers were ground and

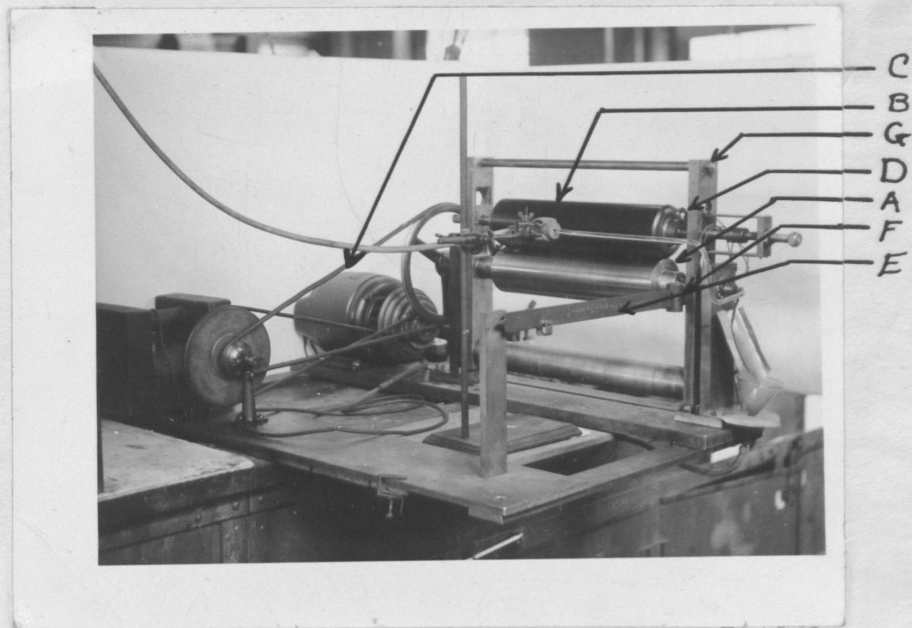


Figure 18.

polished to an accuracy of 0.0001 inch. They were so arranged that the lower roller (A), having a diameter of 7.620 cm., (3.0000 inches), could be driven by an electric motor (C), at eight different rates of speed, ranging from 50 to 480 revolutions per minute. The upper roller (B), having a diameter of 7.897 cm. (3.1090 inches), was driven only by contact with the lower roller, against which it rested. The upper roller thus functioned as a brake on the lower roller.

The lower roller was supported by ball bearings, the upper roller resting of its own weight on the lower roller and held in place by sliding bronze bearings. Both of the

rollers and their bearings were supported by the frame (G), the whole being so balanced that its center of gravity was only a little below the axis of the lower roller. A graduated balance arm was attached to the frame (G). Frame (G) was permitted to swing freely on the shaft of roller (A) and this formed a dynamometer capable of measuring the frictional torque between rollers (A) and (B).

The two rollers were made having different diameters in order to provide for uniform peripheral distribution of the plastic to be tested.

The instrument was equipped with an electrical contact (D) revolution counter whereby the revolutions per minute of the rollers could be easily and accurately counted. The determination of the resistance between the rollers, or the resistance of the ink film splitting between them (hereafter called "Torque"), was made directly by weighting the graduated balance arm (E) by means of a sliding 100 gram weight (F).

Discussion of Results Obtained with the Tackometer.

In the preliminary test with the instrument, the rollers were cleaned and free from oil and grease, and the revolutions per minute of lower and upper rollers were determined at the eight different speeds by the electrical revolution counter. These data are recorded in Table XIX.

Table XIX.

Preliminary Run with Tackometer - Rollers Clean and Dry.

1. Speed	2. R. P. M. of Lower Roller	3. R. P. M. of Upper Roller	4. Calculated R. P. M. of Upper Roller	5. Observed Torque g. cm.
Low 1	53	51	51.1	100
" 2	53 104	51 100	100.4	100
" 3	104 155	100 150	149.6	100
" 4	155 206	150 199	198.8	100
" 5	206 257	199 248	248.0	100
High 3	257 300	248 290	289.6	100
" 4	300 399	290 385	385.0	100
" 5	399 497	385 479	479.2	100
	497	479		

The speed of the upper roller was calculated as follows:

$$S' = \frac{SD}{D'}$$

when S and S' are the speeds of lower and upper rollers respectively, and D and D' are the diameters of the lower and upper rollers respectively. The calculated speed of the upper roller (column 4) agreed very closely with the observed speed (column 3). This indicated that there was no slipping of the upper roller when run dry. The observed torque (column 5) was found to remain constant at all speeds.

In the preliminary work, tests were made on lithographic varnishes, the physical properties of which were known.

A given weight of a sample of varnish (0.50 - 1.00 gram) was placed on the rollers and distributed as uniformly as as possible, this being facilitated by moving the upper roller backward and forward along its axis several times. The motor was started at the low speed (50 R. P. M.), and the speeds of the two rollers, the torque, and the temperature were observed. This procedure was repeated for the other speeds.

The torque reading was considered the most essential and it was hoped that it would give the desired information concerning tack. In addition to this, slippage in centimeters per minute for the upper roller could be calculated from the above data. This was done by determining the peripheral speed of the rollers and subtracting, as:

$7.62 \times \text{R. P. M. lower roller (A)} = \text{peripheral speed of A.}$

$7.897 \times \text{R. P. M. upper roller (B)} = \text{peripheral speed of B.}$

$\text{Peripheral speed of A} - \text{peripheral speed of B} = \text{slippage in cm./min.}$

The percentage of slip was calculated by dividing the slippage in centimeters per minute by the peripheral speed of the lower roller, as:

$$\frac{\text{slippage in cm./min.}}{\text{peripheral speed of lower roller}} \times 100 = \text{percent slip.}$$

In treating the results graphically, the following values were plotted against the revolutions per minute of the lower roller: (1) torque, (2) slippage in cm./min., and (3) percent slip.

Thus at the beginning of this study a #0000 lithographic varnish (see Table I for physical and chemical properties) was tested. Three samples of different weights were run, the weights of the respective samples being 0.2548, 0.5042, and 0.7508 grams. As stated above, the speed of the two rollers, the torque, and the temperature was observed at each of the eight speeds. The results thus obtained are given in Table XX. The slip in cm./min. and the percent slip were calculated and the results recorded in columns (5) and (6) of the same table. The data thus obtained are plotted in Figures 19, 20, and 21. It will be observed that there is an increase in torque with an increase in the weight of the sample. The slip in cm./min., and the percent slip also increased with the increase in film thickness.

The results obtained with the heavier lithographic varnishes (#2 and heavier) were regarded as unreliable, due to the fact that it was impossible to get an even film of varnish on the rollers and hence, are not given. In spite of the fact that the two steel rollers were supposedly machined and ground to an accuracy of 0.0001 inch, it was found that they did not run together perfectly. The result was an uneven film of varnish on the rollers, and consequently the torque varied with the unevenness of the film. In the testing of inks, it was even more difficult to get an even film than it was with the more viscous varnishes. This was very likely due to the plastic nature of the ink.

Table XX.

Preliminary Work:---The Study of a #0000 Varnish.

Experiment 1.

Conditions:----

Specific gravity----0.9551 Temperature-----25 - 26 C.

Absolute viscosity----4.94 Wt. of sample----0.2548 grams.

	1.	2.	3.	4.	5.	6.
	Approximate	R. P. M. of	R. P. M. of	Torque	Slip in	% Slip
	Speed	Lower Roller	Upper Roller		cm./min.	
L	1	53	41	650	251	19.8
L	2	104	89	660	279	12.5
L	3	153	137	640	263	7.18
L	4	203	186	550	234	4.82
L	5	253	235	500	226	3.72
H	3	299	280	460	221	2.94
H	4	398	375	410	224	2.35
H	5	497	467	380	311	2.30

Experiment 2.

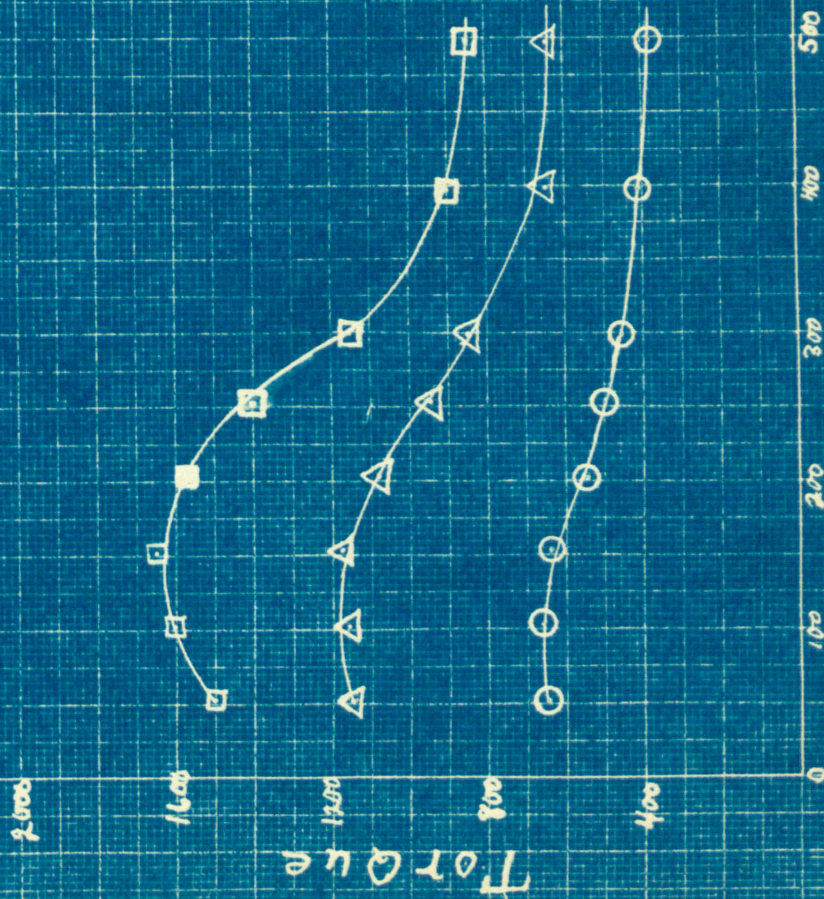
Conditions other than the above:--- Wt. of sample--0.5042 grams.

L	1	52	33	1150	426	35.0
L	2	102	79	1160	482	19.7
L	3	153	126	1175	536	14.6
L	4	203	174	1080	543	11.2
L	5	254	224	950	525	8.64
H	3	299	270	850	460	6.4
H	4	398	367	650	422	4.43
H	5	497	461	650	460	3.88

Experiment 3.

Conditions other than the above:---Wt. of sample--0.7508 grams.

L	1	52	28	1500	534	42.8
L	2	103	73	1600	655	26.5
L	3	152	118	1650	712	19.6
L	4	202	166	1575	718	14.9
L	5	253	216	1400	697	11.5
H	3	299	265	1150	584	8.13
H	4	398	361	900	571	6.00
H	5	497	451	850	708	5.95



R.P.M. Lower Roller

Figure 19.

Results plotted from Table XX

○ = 0.1545 g #0000 varnish
 △ = 5042 g #0000 varnish
 □ = 7508 g #0000 varnish

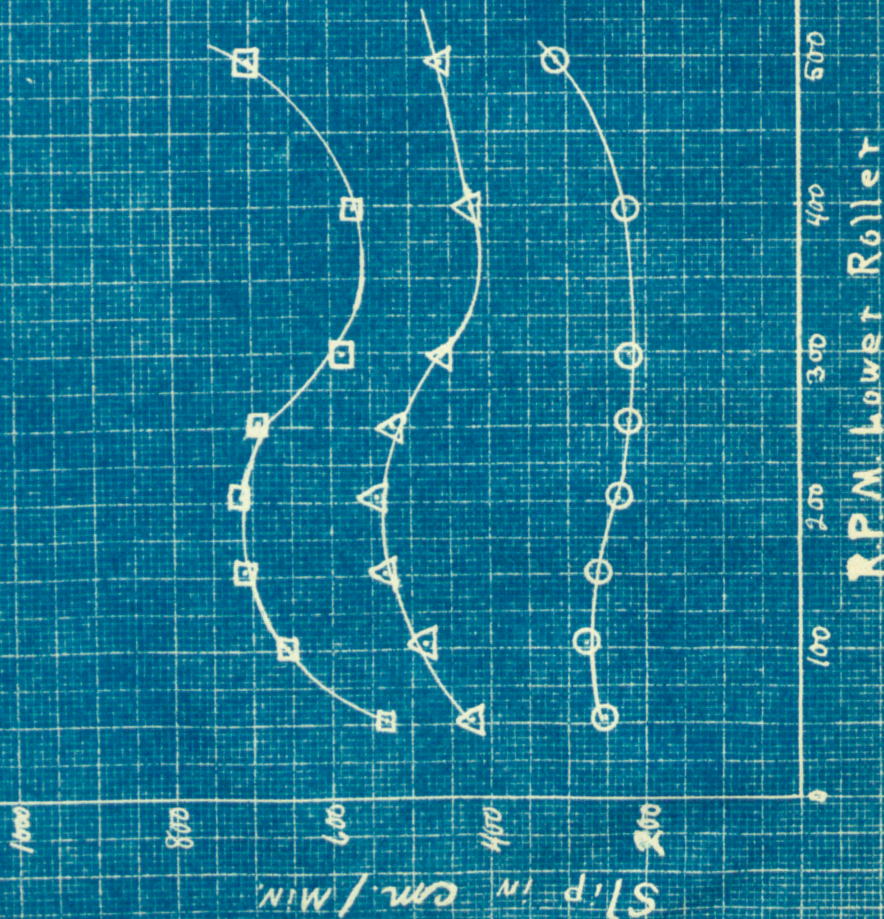
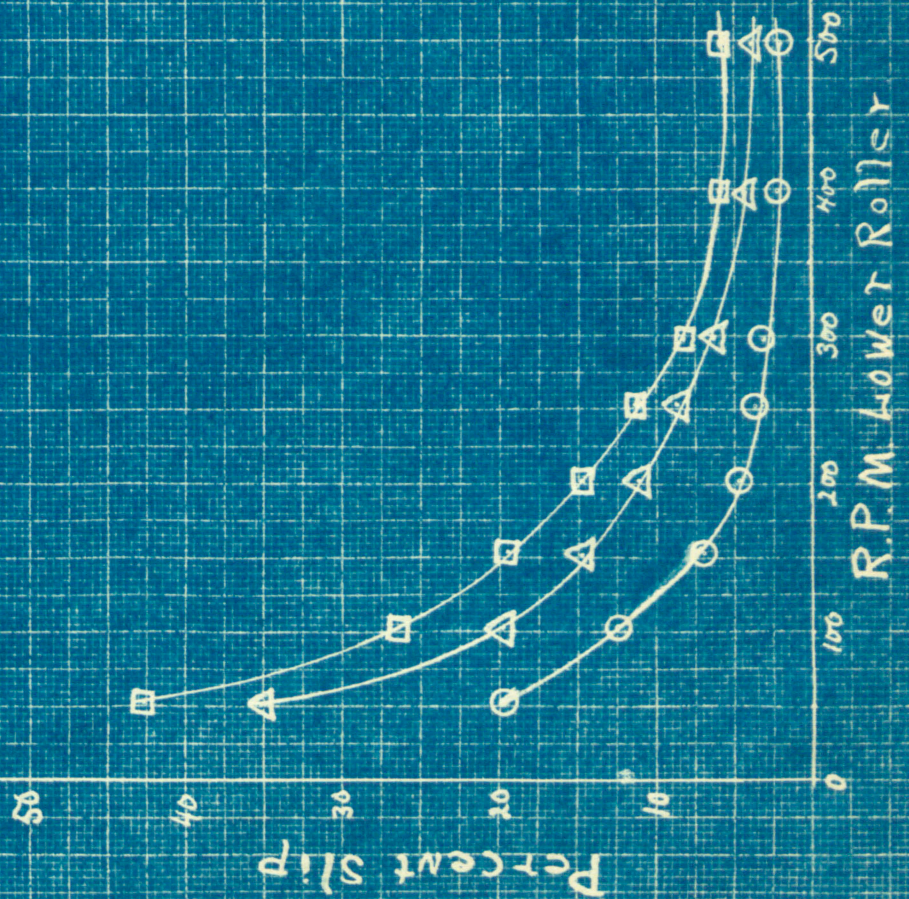


Figure 20.



Results Plotted from Table XX

○ = 0.2548 g #0000 varnish

△ = 5042

□ = 7508

Figure 21.

This difficulty was overcome by replacing the upper steel roller with a resilient roller. This roller had a diameter of 7.925 cm. and was made of vulcanized vegetable oils coated on a steel stock. It contained no rubber, although it had many characteristics of the latter. It was obtained from the Ideal Roller and Manufacturing Company, Chicago, Ill., manufacturers of Ideal Lithographic Rollers. Practically all modern lithographic presses are equipped with this type of ink rollers.

It was with some hesitancy that the change was made, because it was felt that it would be more difficult to duplicate the exact dimensions and resiliency of such a roller than would be the case with steel rollers. It was felt, however, that if at any time, more of the same type of instruments were to be made, a careful calibration would take care of any slight differences that might occur between different rollers.

It was found that by the use of the resilient roller, an even film of a plastic material could be obtained. Another difficulty arose, however, which required some modifications. It was observed that a constant temperature was not maintained during the course of a run. The temperature would rise from 1.5° - 3° centigrade during the 20 - 30 minutes required to make the readings.

The temperature was read from a thermometer which was placed in a mercury well in the end of the lower roller.

It was further observed that check results could not be obtained by repeating the readings. The torque was invariably lower the second time, especially at the lower speeds. The question arose as to whether the decrease in torque was due to the rise in temperature alone, whether it was due to the amount of working received by the ink, or a combination of the two.

In order to settle the question, and to eliminate the temperature variable, it was deemed necessary to devise a method of thermostatic control.

It is to be remembered that the upper roller was mounted in practically frictionless bearings, being driven only by the contact it made with the lower roller. Thus the upper roller functioned as a break on the lower, and it would be impossible to make any alterations that would increase the drag or the resistance on the upper roller without seriously interfering with the torque readings and making them practically valueless.

Due to the fact that the lower roller was the source of power for the instrument, an increase in drag or resistance would make no difference in the torque readings, unless it was large enough to cut down the speed materially.

The decision was made to bore out the lower roller to form a shell, and then to circulate water through it from a constant temperature water bath.

Such an arrangement made it possible to maintain a practically constant temperature during a run. The tempera-

Table XXI.

Preliminary Work:---Run with Resilient Roller and Hollow Cylinder
Cooling Device.---Rollers, Clean and Dry.

1. Approximate Speed	2. R. P. M. of Lower Roller	3. R. P. M. of Upper Roller	4. Calculated R. P. M. of Upper Roller	5. Temp.	6. Observed Torque gm. cm.
L 1	51	49	49.0	25 C.	0
	51	49			
L 2	101	97	97.1	"	"
	101	97			
L 3	150	143	143	"	"
	150	143			
L 4	200	192	192	"	"
	200	192			
L 5	248	238	238	"	"
	248	238			
H 3	300	287	287.4	"	"
	300	287			
H 4	398	379	379.5	"	"
	398	379			
H 5	498	475	475	"	"
	498	475			

ture effect upon the upper resilient roller was considered negligible, due to the fact that it was composed of a material that was a poor conductor of heat. The heat generated during the working of the plastic on the rollers could thus be carried off by the water, and the temperature of the two rollers maintained practically constant.

In the preliminary run, after having made these changes in the lower roller, the rollers were cleaned, and the revolutions per minute of each were determined at the eight different speeds. These data are recorded in Table XXI. As in the previous case, the speed of the upper roller was calculated from the speed of the lower one, and was found

to agree very closely with the observed speed. This showed that there was no slipping of the upper roller when run dry. The torque and temperature readings remained constant during the entire observation.

In making tests on inks with this instrument, it was desirable to use a sample the volume of which would give a film thickness approximately equal to that employed on a lithographic press. It was necessary to make some experimental observations and then calculate the amount of ink required.

This was done by taking a known quantity of ink of known specific gravity and rolling it out on a slab with an ink roller until the desired film in the judgement of an experienced lithographer was obtained. The area over which the ink was spread on the slab, and the area of the roller was calculated. Then from the known volume of ink it was possible to calculate the film thickness of the ink assuming that the ink film splits in the middle at all times. Thus 2.5 c.c. of ink was spread over 1125 sq. cm. of surface on the slab and 940 sq. cm. of surface on the roller, making a total of 2065 sq. cm. Therefore, $2.5000 \text{ c.c.} \div 2065 \text{ sq. cm.} = 0.00121 \text{ cm.}$ or 0.000476 inches, the thickness of the film. This being very close to 0.0005 of an inch, this latter value was used on the rollers.

This value for film thickness agrees very closely with the value as given by R. F. Bowles (27),

(27) Bowles, R. F., - Modern Lithographer, 26, No.12, Dec., 1930, p. 288 - 296.

who says that "if 8000 lithographic impressions were superimposed that the resulting film would be one inch thick". It follows that each individual film would be $1/8000 = 0.000125$ inch thick.

On a lithographic press the ink passes down over the ink rollers from the ink fountain to the plate, from the plate it is transferred to the blanket, and thence to the paper. Providing that the paper gets a film of ink 0.000125 inch thick and assuming that the film breaks in the middle each time, then the blanket has a film 0.000250 inch thick, and the plate has a film 0.0005 inch thick, a value practically identical to the one determined experimentally. Due to the fact that the volume of ink was measured in c.c., the value for film thickness was converted from inches to centimeters. Thus $0.0005 \times 2.54 = 0.00127$ cm.

In calculating the volume of ink to be used on the tackometer, the area of the rollers in sq. cm. was determined. (A) $30.48 \times 7.620 \times = 728$ sq. cm. - area of lower roller. (B) $30.48 \times 7.925 \times = 758.8$ sq. cm. - area of upper roller. Total area of cylinder = 1486.8 sq. cm. $1486.8 \times 0.00127 = 1.88$ c.c. of ink to give the desired film thickness. Then, by multiplying the volume by the density, the weight of the ink to be used was readily determined. The

sample necessary to give the correct film thickness was weighed out on an analytical balance.

In the preliminary work, torque readings were made by starting at the low speeds and gradually increasing to the high speeds. As previously stated, it could not be determined whether the inability to check results upon repeating the tests with the same sample was due to the rise in temperature, or due to the working of the plastic. However, when the temperature was maintained constant and check results could not be obtained, it was definitely proved that the torque readings did change with agitation.

In the light of these results it was obvious that a standardized method would have to be developed in order to give consistent and comparable readings.

A series of eight tests was made as follows: In the first test, a given weight of sample was tested, starting at the lowest speed and increasing, while the second test was made with a similar sample by starting at the highest speed and coming down. The third sample was placed on the rollers and run for 5 minutes at 250 revolutions per minute, and then the torque readings were made at increasing speeds; the fourth sample was treated in a similar way but tested at decreasing speeds. The fifth and sixth samples were run at 250 revolutions per minute for ten minutes and then the torque readings were made at increasing and decreasing speeds. The seventh and eighth samples were run over the ink mill five times and then tested in the same manner as samples 1 and 2.

Table XXII.

Determination of a Standard Method of Testing Inks by the
Use of a Tackometer.

Conditions:-----

Temperature-----25° C.

Wt. sample Test 1.-----2.5962 g.

Wt. sample Test 2.-----2.5973 g.

Ink: S1, #4, used in this study - Density--1.378

	1. Approximate Speed	2. R. P. M. of Lower Roller	3. Torque Test 1	4. Torque Test 2
L	1	50	2450	6100
L	2	99	3450	5600
L	3	146	4000	4950
L	4	194	4500	4500
L	5	238	4800	4100
H	3	296	5200	3700
H	4	392	5600	3100
H	5	480	6000	2200

Conditions other than the above:--

Wt. sample Test 3.-----2.5940 g.

Wt. sample Test 4.-----2.5916 g.

Samples run 5 minutes at 250 R. P. M.

			Test 3	Test 4
L	1	50	2200	6000
L	2	99	3150	5600
L	3	146	3750	4900
L	4	194	4300	4450
L	5	238	4650	4100
H	3	296	5000	3650
H	4	392	5500	3000
H	5	480	6000	2100

Conditions other than the above:--

Wt. sample Test 5.-----2.5996 g.

Wt. sample Test 6.-----2.5922 g.

Samples run 10 minutes at 250 R. P. M.

			Test 5	Test 6
L	1	50	2200	5900
L	2	99	3150	5550
L	3	146	3750	4900
L	4	194	4200	4400
L	5	238	4600	4050
H	3	296	5000	3600
H	4	392	5500	3000
H	5	480	5900	2100

Table XXII. Continued.

Conditions other than the above:--

Wt. sample Test 7.----- 2.5988 g.

Wt. sample Test 8.----- 2.5976 g.

Samples run over the mill 5 times.

Approximate Speed	R. P. M. of Lower Roller	Torque Test 7	Torque Test 8
L 1	50	2100	5900
L 2	99	3050	5500
L 3	146	3750	4900
L 4	194	4200	4400
L 5	238	4500	4050
H 3	296	4900	3650
H 4	392	5400	3000
H 5	480	5900	2100

The results of these tests are given in Table XXII and the data obtained by increasing the speed are plotted in Figure 22. The data obtained by decreasing the speeds are plotted in Figure 23.

It will be observed from the curves in Figure 23 that the more consistent torque readings were obtained by starting at highest speeds and going down. It was concluded from the above test that the best method was the one in which the sample was run for 5 minutes at 250 revolutions per minute and the torque readings made by beginning at the highest speed and going down.

In testing an ink by the standardized method, the procedure was as follows: The weight of ink necessary to give a volume of 1.88 c.c. (calculated from the density of the ink) is spread out evenly on the upper roller. Circulation of

Results Plotted from Table XXII

- INK S.I. - Taken out of container, and tested
- △ Same ink, but run for 5 MIN at 250 R.P.M.
- x over INK mill 5 times

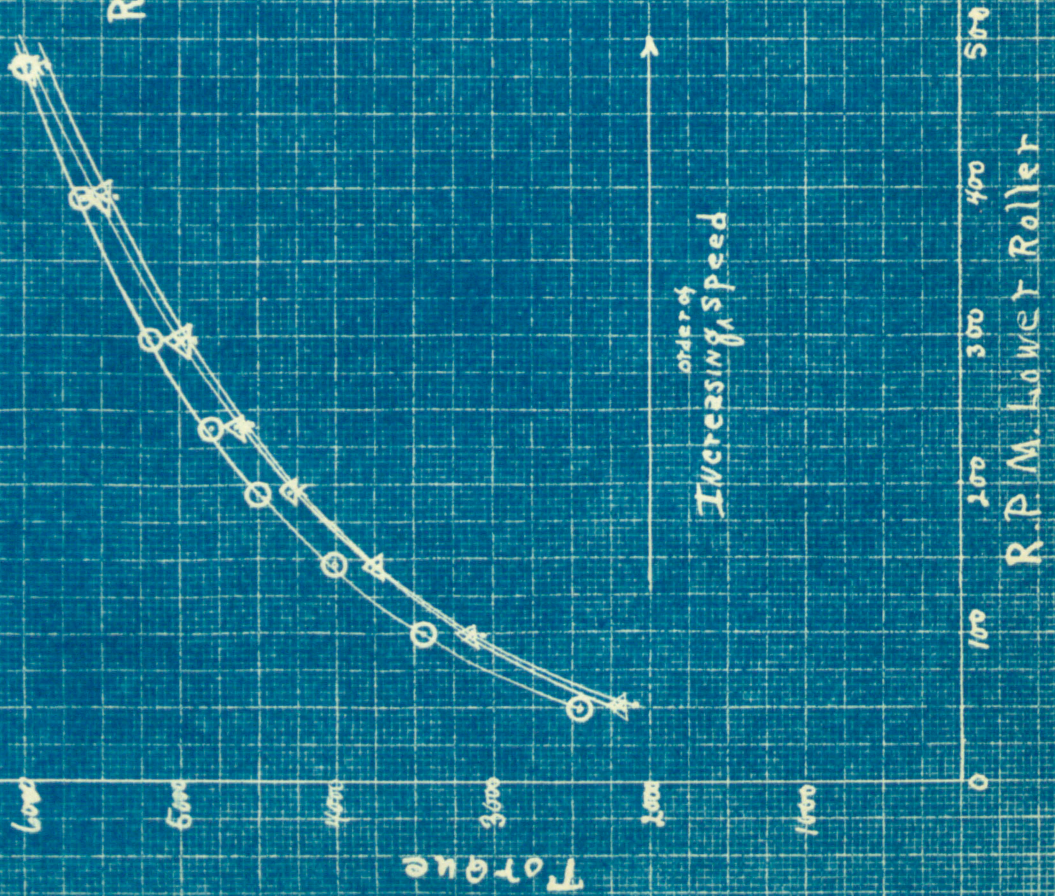
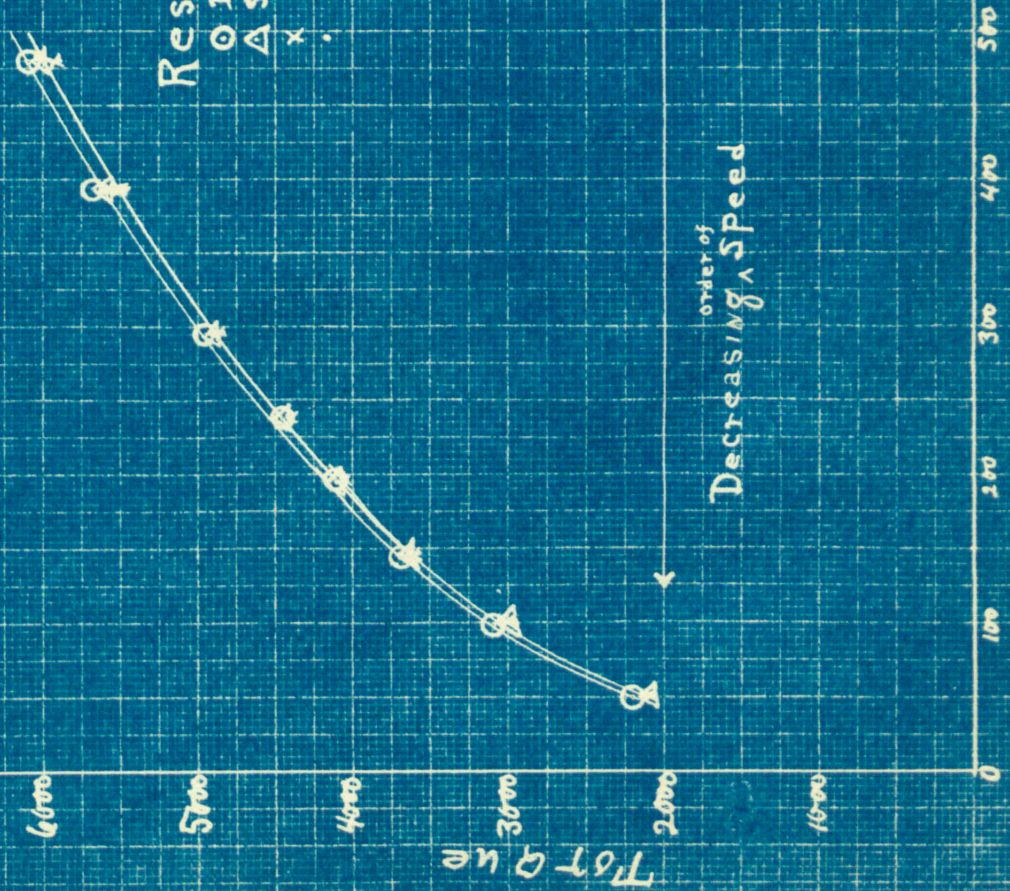


Figure 23.



Results Plotted from Table VIII

○ INK 51 - #4 - Taken out of container, and tested

△ Same INK, but run for 5 min at 250 R.P.M.

x 10 over INK mill 5 times

Decreasing Speed
order of

R.P.M. Lower Roller

Figure 23.

water through the lower cylinder is started. The rollers are then turned slowly by hand until the ink appears to be evenly distributed. The rollers are then driven at 250 revolutions per minute for 5 minutes, during which time the upper roller is moved back and forth along its axis to further the attainment of an even film. At the end of 5 minutes the speed is changed to the high speed (480 R. P. M.) and run for 1.5 minutes, the torque reading is then made during the next 30 seconds. It required about 30 seconds to change to the next lower speed where the same procedure is repeated. Therefore, the total time required to make eight readings in the testing of an ink is about 25 minutes.

In the making of a test, it was believed that this treatment of the ink was the nearest approach to the procedure used in preparing an ink to be run on a press. It is very seldom that an ink is run over the ink mill before being used. The usual procedure is to take the ink from its container, work it on a stone slab with a long ink spatula for 5 minutes or longer. Sometimes reducers and driers are added depending on the concentration and type of ink. In such a case the ink must be worked again until the new materials are evenly distributed. The ink is then placed in the ink fountain and run. Thus the method of placing the sample on the rollers and running them for 5 minutes at 250 revolutions per minute is comparable to the preliminary treatment the ink received, previous to being run on the press.

A Study of the Effect of Temperature.

The effect of temperature on the tackometer readings was next studied. Three separate samples of equal weights of the same ink were tested under identical conditions, except that the temperature of the lower roller was maintained at 15°, 25°, and 35° C. during the testing. The data obtained by carrying out this series of experiments are given in Table XXIII, and the results shown graphically in Figure 24. The work was repeated and the results checked as shown in Table XXIV and Figure 25.

An inspection of the graphical representations of these results (Figures 24 and 25) show that the lower parts of the three curves are in the relative positions that one would expect. However, the upper part of the curve at 15 C. is considerably out of place. Apparently what happened was that the ink became shorter and less mobile, which is the same as saying "that it developed a higher yield value and less tendency to flow".

At this temperature and especially at the higher speeds there was a strong tendency for this ink to form ridges running around the rollers which evidently reduced the area of contact and therefore reduced the frictional energy. This would account for the peculiar character of the curves obtained at 15 C.

It is interesting to note that the slip in centimeters per minute of the upper roller, and the percent slip as shown in Table XXIII are very much less than the corresponding

Table XXIII.

Study of Temperature Effect. - Tackometer.

Conditions:----

Volume of ink-----1.88 c.c.

Density of ink-----1.1479

Wt. sample-----2.1581 g.

Temperature constant---15 C.

Run for 5 minutes at 250 R. P. M. before testing.

1.	2.	3.	4.	5.	6.
Approximate Speed	R. P. M. of Lower Roller	R. P. M. of Upper Roller	Torque	Slip in cm./min.	% Slip
H 5	480	456	6600	125	1.09
H 4	386	367	6600	100	1.08
H 3	292	278	6600	75	1.18
L 5	226	215	6600	75	1.38
L 4	175	165	6600	75	1.78
L 3	126	119	6600	60	1.90
L 2	80	75	6000	50	2.52
L 1	38	36	5000	25	2.75

Conditions other than the above:--Temperature constant--25 C.

H 5	480	455	7100	170	1.52
H 4	381	360	6800	158	1.11
H 3	293	275	6500	147	2.28
L 5	228	217	6250	122	1.38
L 4	176	165	6000	100	2.39
L 3	127	119	5500	92	2.48
L 2	88	82	4900	67	3.07
L 1	46	42	3500	93	4.55

Conditions other than the above:--Temperature constant--35 C.

H 5	483	453	6200	280	2.43
H 4	388	366	5600	176	2.15
H 3	295	278	5000	142	2.12
L 5	233	218	4600	157	2.70
L 4	186	174	4100	121	2.81
L 3	141	132	3700	89	2.63
L 2	97	90	2900	81	2.81
L 1	50	47	2000	28	2.34

Table XXIV.

Study of Temperature Effect. - Tackometer.

Conditions same as in Table XXIII except Temperature constant-15 C.

Approximate Speed	R. P. M. of Lower Roller	R. P. M. of Upper Roller	Torque	Slip in cm./min.	% Slip
H 5	483	461	6600	100	0.871
H 4	389	368	6600	150	1.61
H 3	292	279	6600	75	1.07
L 5	228	215	6600	100	1.84
L 4	173	164	6600	75	1.80
L 3	123	116	6600	50	1.76
L 2	79	74	6200	50	2.65
L 1	40	37	5000	30	3.14

Conditions other than the above:--Temperature constant--25 C.

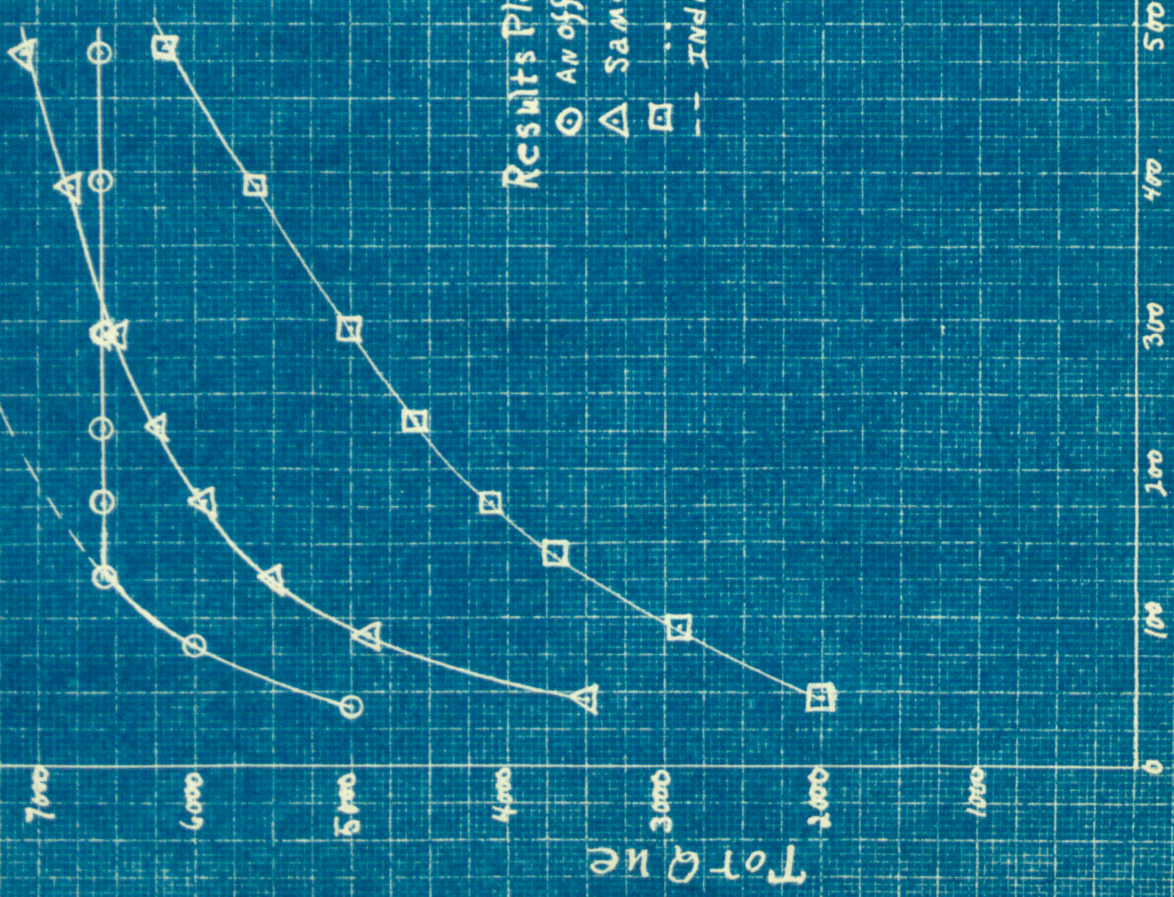
H 5	482	457	7200
H 4	387	367	6900
H 3	294	278	6600
L 5	227	211	6300
L 4	178	164	6150
L 3	131	124	5700
L 2	89	83	5000
L 1	46	42	3500

Conditions other than the above:--Temperature constant--35 C.

H 5	483	456	6400
H 4	390	366	5700
H 3	298	289	5000
L 5	239	224	4600
L 4	191	178	4300
L 3	144	135	3800
L 2	97	91	3200
L 1	50	47	2200

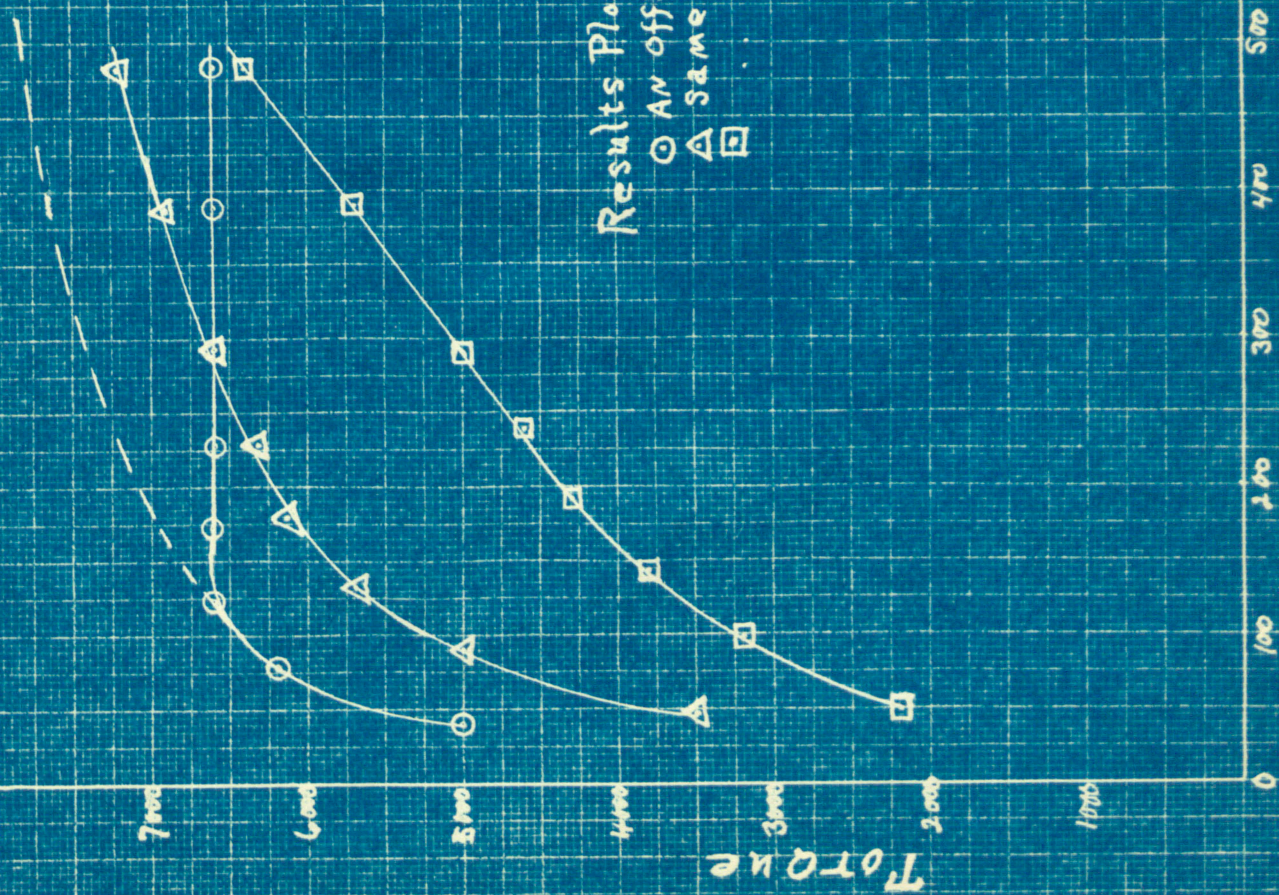
Results Plotted from Table XXIII

- AN Offset Process black, tested at 15°C.
- △ Same INK --- 25°C
- --- 35°C
- INDICATES upper part (Theoretical) of curve at 15°C.



R.P.M. Lower Roller

Figure 24.



Results Plotted from Table XXIV

○ AN offset Process black — tested at 15°C.
 △ Same INK — .. 25°C.
 □ .. 35°C.

R.P.M. Lower Roller

values obtained with #0000 lithographic varnish as given in Table XX. It will be observed that the percent slip in the case of the lithographic ink is practically negligible at the high speeds, and increases slightly at the lower speeds.

Study of the Effect of Film Thickness.

A study was made to determine the effect of variation of film thickness on the torque readings, all other conditions being constant. In carrying out this study four samples were tested, the weights of the respective samples being 0.2500, 1.0000, 2.158, and 4.0000 grams. The film thickness represented by these weights are in the order given: 0.000146, 0.000586, 0.00127, and 0.002334 centimeters.

The experimental data thus determined by testing the samples of the above film thickness are given in Table XXV, and the results plotted in Figure 26. It can be seen that the increase in film thickness results in an increase in torque up to a maximum film thickness and then a further increase causes a decrease in torque. Just why this should occur cannot be explained at present, but will require further research.

The four series of inks in which the proportions of pigment and vehicle (see Formulas on page 82) were varied and which had been tested by the plastometer were also tested by the tackometer. The data thus obtained are given in Tables XXVI, XXVII, XXVIII, and XXIX. The torque readings are plotted against the speed of the lower roller in Figures 27, 28, 29, and 30.

Table XXV.

A Study of the Effect of Film Thickness.

Conditions:---

Temperature-----25 C.

Density of ink-----1.1479

Wt. of sample-----0.2500 g.

Film thickness-----0.000146 cm. -----0.000057 in.

Samples run at 250 R. P. M. for 5 minutes before testing.

Approximate Speed	R. P. M. of Lower Roller	R. P. M. of Upper Roller	Torque	Slip in cm./min.	% Slip
H 5	482	459	6800	125	1.09
H 4	386	367	6550	125	1.35
H 3	294	279	6300	100	1.42
L 5	228	215	6050	100	1.86
L 4	181	170	5800	100	2.33
L 3	131	123	5600	75	2.40
L 2	89	83	5000	50	2.36
L 1	46	43	3600	30	2.72

Conditions other than the above:---

Wt. of sample-----1.00000 g.

Film thickness-----0.000586 cm. -----0.000230 in.

H 5	483	457	7300	200	1.74
H 4	385	366	7100	100	1.09
H 3	293	279	6800	75	1.07
L 5	228	217	6500	60	1.11
L 4	182	171	6200	100	2.30
L 3	134	125	5800	100	3.19
L 2	88	82	5100	50	2.36
L 1	46	43	3600	36	3.20

Conditions other than the above:---

Wt. of sample-----2.1581 g.

Film thickness-----0.00127 cm. -----0.0005 in.

H 5	480	455	7100	175	1.52
H 4	381	363	6800	100	1.11
H 3	293	275	6500	160	2.28
L 5	228	217	6250	75	1.38
L 4	176	165	6000	100	2.39
L 3	127	119	5500	75	2.48
L 2	88	82	4900	65	3.07
L 1	46	42	3500	60	4.55

Table XXV. - Continued.

Conditions other than the above:---

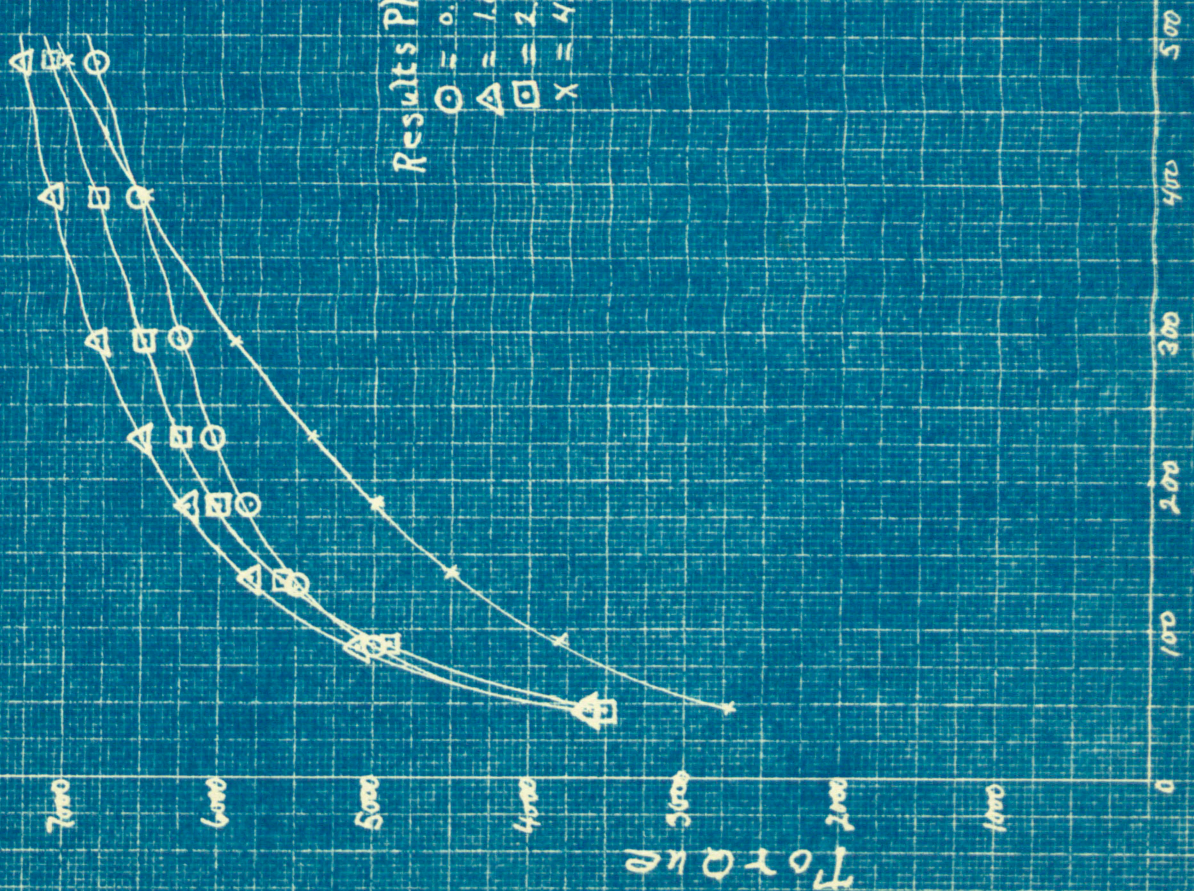
Wt. of sample-----4.0000 g.

Film thickness-----0.002334 cm. -----0.000923 in.

Approximate Speed	R. P. M. of Lower Roller	R. P. M. of Upper Roller	Torque	Slip in cm./min.	% Slip
H 5	478	450	7000	250	2.17
H 4	387	364	6500	200	2.16
H 3	293	276	5900	150	2.13
L 5	230	213	5400	200	3.59
L 4	182	170	5000	125	2.86
L 3	137	128	4500	100	3.29
L 2	93	87	3800	50	2.24
L 1	48	44	2700	50	4.35

It will be observed from both the tables and the curves that there is an increase in the torque reading as the concentration of the pigment was increased in each individual series.

It was observed that Ink #1, Series I, gave the same torque readings as Ink #3, Series IV. It was believed that the reason for this was that Ink #1, Series I, which had been prepared first, had aged until it had practically the same consistency as the Ink #3, Series IV. Two new inks were made up, using the same amounts of the same materials as were used in compounding the first inks. These inks were tested immediately after being prepared and the results are given in Table XXX, and the results were plotted in Figure 31. It can be seen that the two freshly prepared inks, differ from each other. In the case of the original inks,



R.P.M. Lower Roller

Table XXVI.

Tackometer Results Obtained with Inks of Series I.

Ink 1.

1. Approximate Speed	2. R. P. M. of Lower Roller	3. Torque	Conditions:-----
			Volume of ink used--1.88 c.c.
			Temp. constant----25.0 C.
			Density of ink--1.300
			Samples run for 5 minutes
			at 250 R. P. M. before
			testing.
			Wt. sample----2.4639 g.
H 5	492	3300	
H 4	394	3100	
H 3	297	2800	
L 5	247	2700	
L 4	198	2550	
L 3	149	2400	
L 2	100	2000	
L 1	51	1500	

Ink 2.

			Conditions other than Above:-
			Density of ink--1.352
			Wt. sample-----2.5422 g.
H 5	491	4150	
H 4	393	3900	
H 3	297	3700	
L 5	246	3450	
L 4	198	3200	
L 3	149	2900	
L 2	100	2500	
L 1	51	1900	

Ink 3.

			Conditions other than above:-
			Density of ink--1.368
			Wt. sample-----2.5810 g.
H 5	491	5150	
H 4	393	4950	
H 3	297	4700	
L 5	246	4500	
L 4	198	4250	
L 3	149	3800	
L 2	100	3300	
L 1	51	2500	

Ink 4.

			Conditions other than above:-
			Density of ink--1.378
			Wt. sample-----2.6240 g.
H 5	484	5800	
H 4	391	5600	
H 3	296	5400	
L 5	244	5200	
L 4	192	4900	
L 3	145	4500	
L 2	99	3800	
L 1	50	2900	

Table XXVI. - Continued.

1. Approximate Speed	2. R. P. M. of Lower Roller	3. Torque	Ink 5. Conditions other than the above;- Density of ink----1.449 Wt. sample-----2.7275 g.
H 5	484	6600	
H 4	387	6400	
H 3	295	6150	
L 5	238	5900	
L 4	184	5700	
L 3	137	5400	
L 2	92	4800	
L 1	48	3700	

Table XXVII.

Tackometer Results Obtained with Inks of Series II.

1. Approximate Speed	2. R. P. M. of Lower Roller	3. Torque	Ink 1. Conditions:----- Volume ink used---1.88 c.c. Temp. constant---25.0 C. Density of ink----1.263 Wt. sample-----2.3528 g. Samples run for 5 minutes at 250 R. P. M. before testing.
H 5	492	3800	
H 4	394	3600	
H 3	297	3300	
L 5	247	3100	
L 4	198	2900	
L 3	149	2550	
L 2	100	2200	
L 1	50	1700	

Ink 2.

1.	2.	3.	Conditions other than above:- Density of ink----1.269 Wt. sample-----2.3787 g.
H 5	490	4900	
H 4	394	4350	
H 3	297	3850	
L 5	247	3650	
L 4	198	3350	
L 3	149	3000	
L 2	100	2600	
L 1	50	1900	

Table XXVII. - Continued.

Ink 3.

1.	2.	3.	
Approximate	R. P. M. of	Torque	Conditions other than above:-
Speed	Lower Roller		Density-----1.288
			Wt. sample---2.4189 g.

H	5	488	5600
H	4	394	5200
H	3	296	4800
L	5	247	4500
L	4	197	4150
L	3	148	3700
L	2	100	3200
L	1	50	2300

Ink 4.

H	5	480	5850	Conditions other than above:- Density-----1.315 Wt. sample---2.4442 g.
H	4	391	5600	
H	3	296	5250	
L	5	244	5000	
L	4	196	4700	
L	3	146	4250	
L	2	96	3700	
L	1	49	2800	

Ink 5.

H	5	480	6500	Conditions other than above:- Density-----1.327 Wt. sample---2.4898 g.
H	4	390	6200	
H	3	295	5800	
L	5	238	5600	
L	4	184	5400	
L	3	137	5100	
L	2	92	4500	
L	1	48	3450	

Table XXVIII.

Tackometer Results Obtained with Inks of Series III.

Ink 1.

1. Approximate Speed	2. R. P. M. of Lower Roller	3. Torque	Conditions:-----
			Volume of ink used--1.88 c.c.
			Temp. constant----25.0 C.
			Density of ink----1.1813
			Wt. sample-----2.1221 g.
			Samples run for 5 minutes at 250 R. P. M. before testing.
H 5	490	5750	
H 4	393	5500	
H 3	297	5100	
L 5	247	4900	
L 4	198	4600	
L 3	149	4200	
L 2	100	3600	
L 1	50	2600	

Ink 2.

H 5	490	6250	Conditions other than above:-
H 4	393	5800	Density of ink--1.1915
H 3	297	5400	Wt. sample-----2.2384 g.
L 5	247	5200	
L 4	198	4800	
L 3	149	4450	
L 2	100	3750	
L 1	50	2750	

Ink 3.

H 5	488	6600	Conditions other than above:-
H 4	392	6100	Density of ink--1.216
H 3	296	5600	Wt. sample-----2.2900 g.
L 5	247	5300	
L 4	197	5000	
L 3	148	4600	
L 2	100	4000	
L 1	50	2900	

Ink 4.

H 5	480	7700	Conditions other than above:-
H 4	391	7100	Density of ink--1.237
H 3	296	6500	Wt. sample-----2.3296 g.
L 5	244	6200	
L 4	196	5800	
L 3	146	5300	
L 2	96	4450	
L 1	49	3400	

Table XXVIII. - Continued.

Approximate Speed		R. P. M. of Lower Roller	Torque	Ink 5. Conditions other than above:- Density of ink--1.260 Wt. of sample---2.3621 g.
H	5	480	8100	
H	4	390	7550	
H	3	295	7000	
L	5	238	6600	
L	4	184	6100	
L	3	137	5600	
L	2	92	5000	
L	1	48	3800	

Table XXIX.

Tackometer Results Obtained with Inks of Series IV.

Approximate Speed		R. P. M. of Lower Roller	Torque	Ink 1. Conditions:--- Volume ink used---1.88 c.c. Temp. constant---25.0 C. Density of ink---1.2410 Wt. sample-----2.3404 g. Samples run for 5 minutes at 250 R. P. M. before testing.
H	5	492	2350	
H	4	394	2200	
H	3	297	2000	
L	5	247	1900	
L	4	198	1750	
L	3	149	1600	
L	2	100	1400	
L	1	50	1000	

				Ink 2. Conditions other than above:- Density of ink--1.252 Wt. sample-----2.3585 g.
H	5	490	2700	
H	4	394	2500	
H	3	297	2300	
L	5	247	2200	
L	4	198	2000	
L	3	149	1850	
L	2	100	1600	
L	1	50	1200	

				Ink 3. Conditions other than above:- Density of ink--1.271 Wt. sample-----2.3919 g.
H	5	488	3300	
H	4	394	3100	
H	3	296	2900	
L	5	247	2750	
L	4	197	2600	
L	3	148	2350	
L	2	100	2050	
L	1	50	1500	

Table XXIX. - Continued.

Ink 4.

1. Approximate Speed	2. R. P. M. of Lower Roller	3. Torque	Conditions other than above:- Density of ink--1.285 Wt. sample-----2.4365 g.
H 5	480	3950	
H 4	390	3700	
H 3	296	3300	
L 5	244	3150	
L 4	196	2900	
L 3	146	2600	
L 2	96	2300	
L 1	49	1750	

Ink 5.

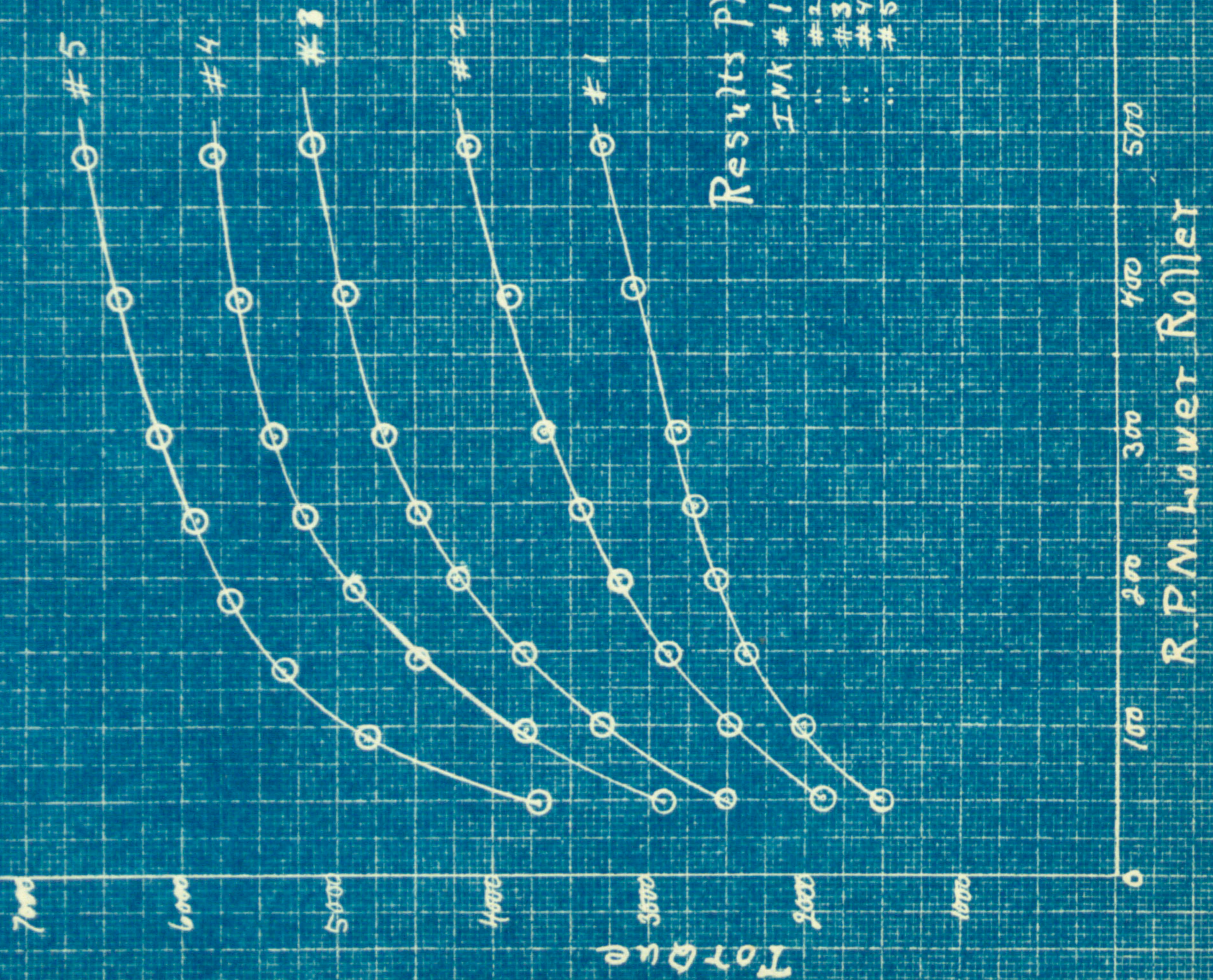
H 5	480	4500	Conditions other than above:-
H 4	390	4300	Density of ink--1.309
H 3	295	4000	Wt. sample-----2.4634 g.
L 5	238	3750	
L 4	184	3500	
L 3	137	3100	

Ink 1'.

H 5	492	3100	Conditions other than above:-
H 4	394	2800	Density of ink--1.303
H 3	297	2500	Wt. sample-----2.4603 g.
L 5	247	2300	
L 4	198	2100	
L 3	149	1900	
L 2	100	1550	
L 1	51	1100	

Ink 3'.

H 5	490	3300	Conditions other than above:-
H 4	392	3075	Density of ink--1.271
H 3	297	2800	Wt. sample-----2.3923 g.
L 5	247	2550	
L 4	198	2300	
L 3	149	2100	
L 2	100	1750	
L 1	51	1300	



Results plotted from Table XXVI - Series I
 Ink #1 - Conformation given on page 82

#2
 #3
 #4
 #5

Figure 27.

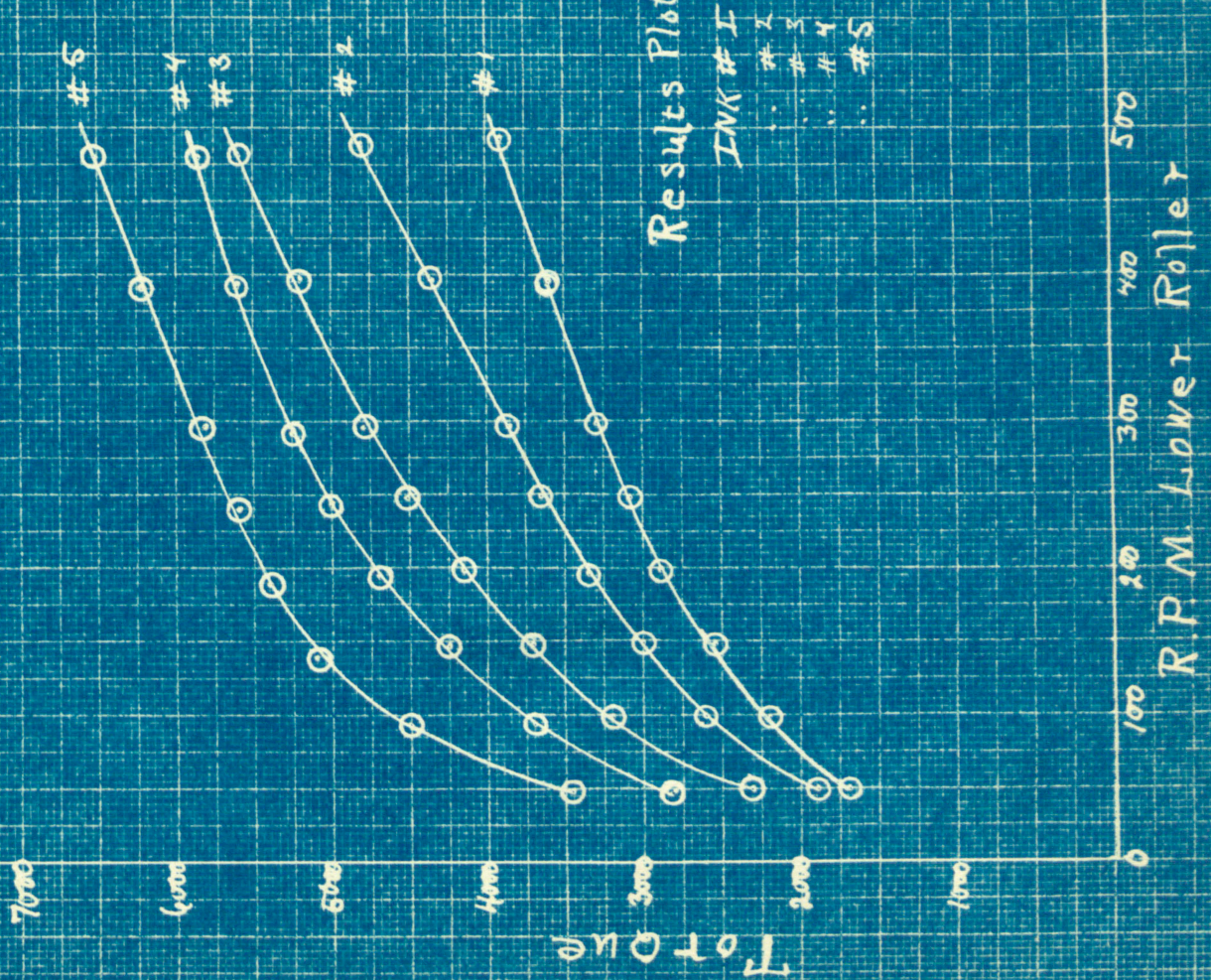
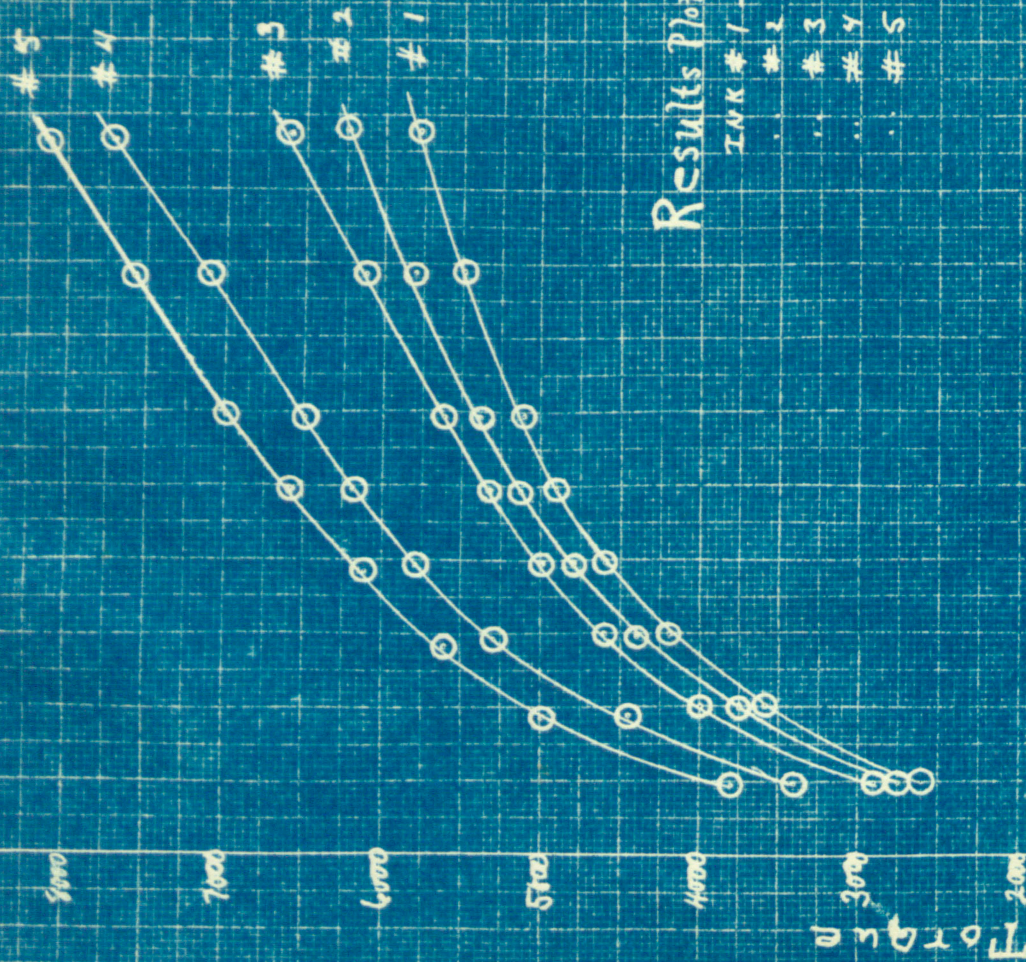


Figure 28.



Results Plotted from Table ~~XXIV~~ -- Series III

INK #1 - Composition given on page 82

#2

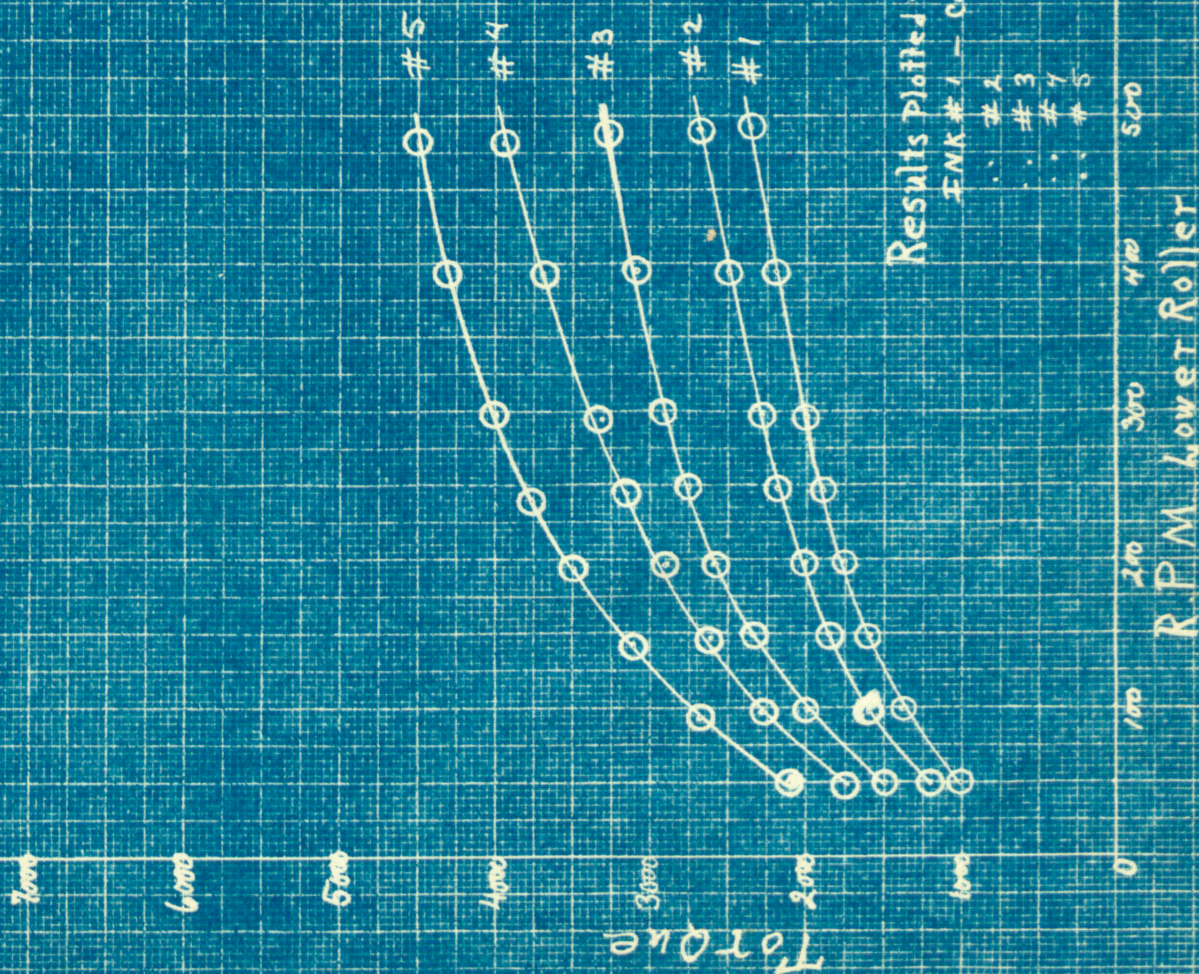
#3

#4

#5

R.P.M. Lower Roller

Figure 29.



Results plotted from Table XXX - Series IV
 ENK #1 - Composition given on page 82

#2
 #3
 #4
 #5

Figure 30.

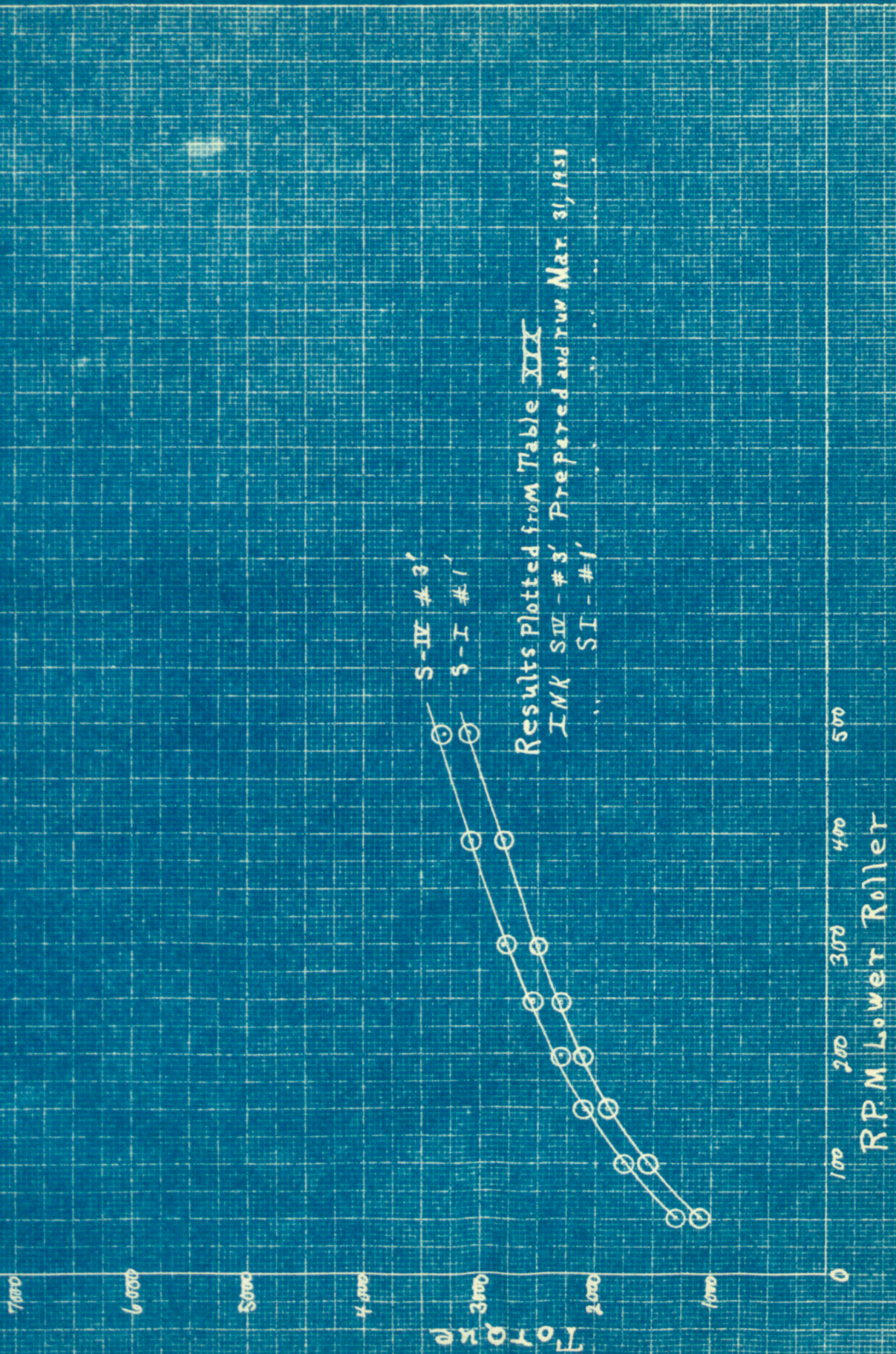


Figure 31.

Series I was made up on Jan. 28, 1931, while Series IV was made up nearly a month later, on Feb. 25, 1931. It is conceivable in the light of the plastometer results that Ink 1, Series I aged sufficiently during the month previous to the preparation of Ink 3, Series IV, that they both appeared to have the same consistency when tested with the tackometer. As can be seen from Figure 31, there is no great difference between the two freshly prepared inks, and that if Ink 1, Series I, was allowed to age for a month, it could readily reach a consistency equal to that of the freshly prepared Ink 3, Series IV. Hence, it was noted that the energy consumed in working an ink in this manner, that the short inks gave curves which were very similar to the curves of long inks. Thus this method seemed to fail to distinguish between a long and short ink.

This illustrates very well how the standards of an ink maker can change and drift. In making up a batch of ink for a customer, he will take out a sample and keep it for further reference. A couple of months, or perhaps a year later, he will get a re-order for some more of the same ink.

The ink maker will get out the original sample, work it over, and then make up the new batch in comparison to the same consistency, using the original sample as the standard. The odds are on the side that the ink has aged during the lapse of time, unless, of course, there are a limited number of components in the ink, and the pigment is an exceptionally inert one.

At any rate, the use of an instrument such as this tackometer in the testing of inks would eliminate any aging effect, and do away with the necessity of having a lot of different samples around. The ink could be tested immediately after preparation by the tackometer, the results recorded as numerical values, and plotted as a curve. These data could then be filed away for future reference in the compounding of duplicate inks.

The next work was to study the effects of various greasy and oily substances that are commonly used as reducers in lithographic inks. In this study, Ink 4, Series I, was used. Three samples of the original ink were respectively reduced by adding 5% Petrolatum, 5% #000 varnish, and 5% #7 varnish. The three reduced inks were compared with the original ink by the finger test method. The results were as follows:

	Original Ink #4, Series I	Same + 5% Petrolatum	Same + 5% #000 Varnish	Same + 5% #7 Varnish
Length	2	3	1	4
Tack	2	4	3	1
Mobility	3	1	2	4

Thus, from these results it can be seen that the petrolatum reduced the length and tack, but increased the mobility. The #000 varnish increased the length and mobility, but reduced the tack. The #7 varnish reduced the length and mobility considerably, but increased the tack.

Samples of these four inks were than tested with the tackometer. The results are given in Table XXXI, and the data plotted in Figure 32. It will be observed from the curves (Figure 32) that Ink containing the #7 varnish, being the tackiest, did not give the highest torque readings as would be expected. This was due to the fact that it was also the shortest. It is typical of the short inks (see Figure 24) to give a flat curve. The other samples come in the right order of tackiness as indicated by the finger tests. As previously observed, the tackometer is not applicable in testing of inks which differ greatly in length. It is apparent that further^{work} will have to be done in the study of relation of length to tack.

Some additional work was done in studying inks as they were obtained from the ink manufacturer, and then reducing them with various materials commonly employed by pressmen. A sample of an offset process black ink, obtained from the International Printing Ink Corporation was used in this study. Two samples of the original ink were reduced by adding respectively 5% #00 varnish, and 5% petrolatum. These reduced inks were then compared with the original ink by the finger test methods, the results being as follows:

	Original Black; as taken from container	Same + 5% #00 Varnish	Same + 5% Petrolatum
Length	1	3	2
Tack	1	2	3
Mobility	3	2	1

It will be observed that the #00 varnish reduces both the length and tack, and increases the mobility. The same is true of the petrolatum, only the increase in mobility is greater.

The original ink was tested on the tackometer in comparison with the reduced inks. The results of these tests are given in Table XXXII and the data shown graphically in Figure 33. It will be observed from the curves drawn for the three inks that they are arranged in the proper order of their tack. The original ink being the tackiest, gives the highest torque readings, the sample containing the #00 varnish is second, while the one containing the petrolatum is third. It will also be observed that the two reduced inks have nearly the same tackiness at the low rates of shear, but show a greater difference at the higher rates of shear.

The deductions and conclusions drawn from the above observations are not to be taken as fully authoritative because they are based on a too limited number of experiments. It is gratifying, however, to find the results indicating that the investigators are proceeding in the right direction.

That the ink manufacturer is in need of scientifically correct methods of testing and controlling the consistency of inks, is illustrated by two samples of offset process black ink received at different times from a reliable ink manufacturer. The two inks were supposed to be identical in working properties.

Table XXXI.

Study of the Effect of Various Greasy and Oily Reducers
on Lithographic Inks.

Conditions:-----

Volume of ink-----1.88 c.c. Average density-----1.378
Wt. sample-----2.5935 g.
Run for 5 minutes at 250 R. P. M. before testing.

	1.	2.	3.	4.	5.	6.
	Approximate Speed	R. P. M. of Lower Roller	Torque of Original Ink	Torque of Same Ink + 5% Petro- latum.	Torque of Same Ink + 5% #000 Varnish.	Torque of Same Ink + 5% #7 Varnish.
H	5	480	5900	4400	4450	4500
H	4	392	5500	4000	4150	4250
H	3	296	4900	3500	3700	4000
L	5	238	4450	3250	3400	3800
L	4	194	4050	3000	3150	3600
L	3	146	3550	2700	2850	3300
L	2	99	3000	2300	2400	2850
L	1	50	2150	1500	1600	2000

Table XXXII.

Further Study of the Effect of Reducers on Inks Obtain-
ed from Inkmakers.

Conditions:-----

Volume of ink-----1.88 c.c.
Average density-----1.1286
Wt. sample-----2.1078 g.
Run for 5 minutes at 250 R. P. M.
before testing.

	1.	2.	3.	4.	5.
	Approximate Speed	R. P. M. of Lower Roller	Torque of Original Black	Torque of Same Ink + 5% #00 Varnish.	Torque of Same Ink + 5% Petro- latum.
H	5	480	6900	6000	5500
H	4	392	6500	5550	5200
H	3	294	5900	4950	4800
L	5	240	5500	4600	4450
L	4	195	5100	4250	4200
L	3	146	4650	3850	3750
L	2	99	4000	3300	3200
L	1	50	2900	2250	2200

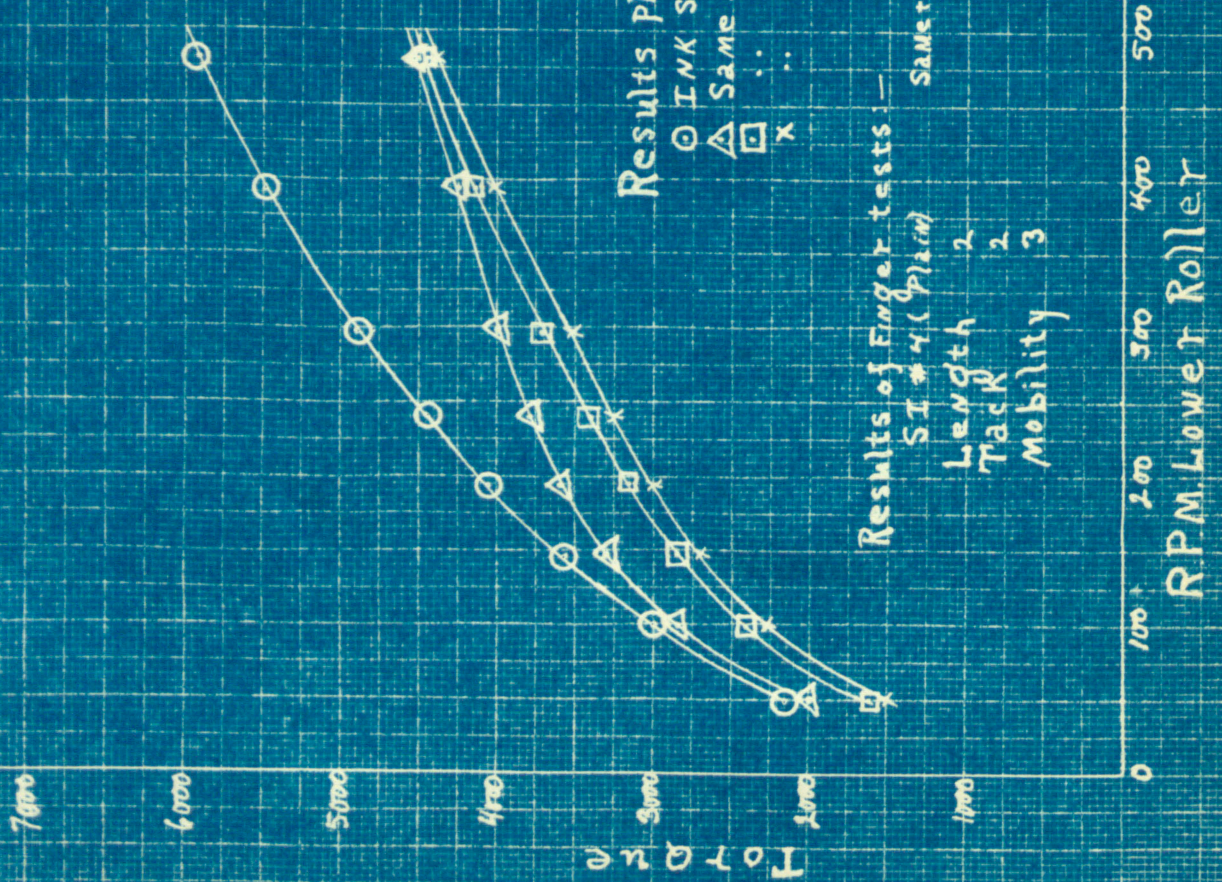
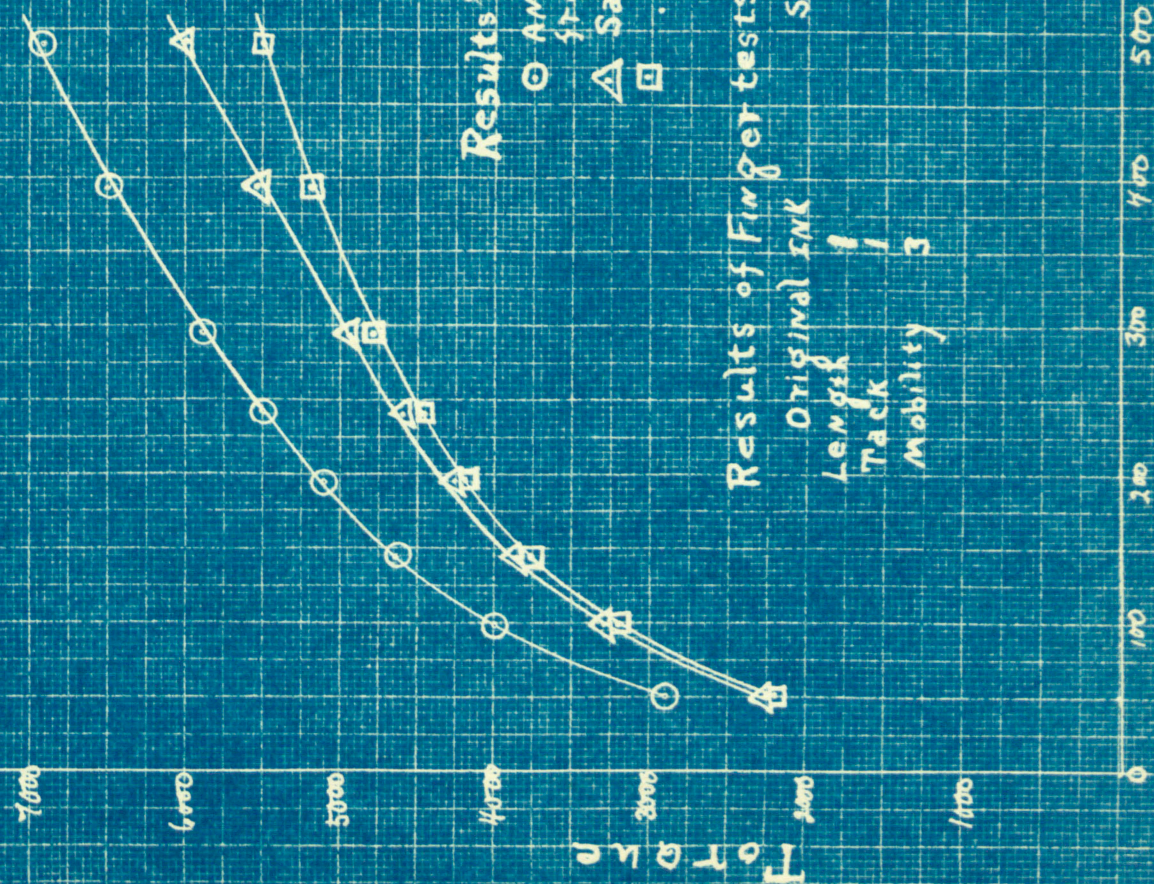


Figure 32.



Results Plotted from Table XXXI

○ An Offset Process black as taken from container

△ Same Ink + 5% #00 Varnish

□ Same Ink + 5% Petrolatum

Results of Finger tests:-

Original Ink

Length 1

Tack 1

Mobility 3

Same + 5% #00 Varnish

3

1

2

Same + 5% Petrolatum

2

3

1

R.P.M. Lower Roller

Figure 37.

The first lot was received June 20, 1931, and the second lot was received sept. 24, 1931. The specific gravities of the two inks were determined, and equal volumes were tested by running on the tackometer. The results of the tests are given in Table XXXIII, and the data plotted in Figure 34. It will be observed that the ink received Sept. 24 is much more mobile or softer, and is not as tacky as the ink received June 20th.

As previously stated, the ink manufacturer keeps a sample of the original ink as a standard for future comparison. In making up a new batch of the same ink, he compares a sample of the new ink with that of the old sample. Due to the fact that the old ink may have acquired considerable set due to ^{standing}~~settling~~, he makes the new ink more mobile and softer than the old standard. It is at this point that experience on the part of the ink maker plays an important part, or where it may be that it is an advantage to be a good guesser.

In the past, the pressmen have been willing to accept inks that vary over quite a wide range in consistency. The only requirement being that the ink be more concentrated than is usually run on the press. The ink makers being aware of this, have been able to get by with finger test measurements of control.

It is admitted that the amount of work done with the tackometer is not sufficient to make it fool proof or to make it safe to say "that this instrument is a cure for all the evils

of the ink maker and the printer". It is felt, however, that it is a step in the right direction, but that further research is necessary before it can be considered a practical control instrument.

Table XXXIII.

Results Obtained with Tackometer in Testing Offset Process

Black Inks of Lots I and II.

Conditions:-----

Volume of ink-----1.88 c.c.

Temperature-----25 C.

Density of ink-----1.1304

Wt. of sample-----2.1208 g.

Run at 250 R. P. M. for 5 minutes
before testing.

Lot I received June 20, 1931.

	1. Approximate Speed	2. R. P. M. of Lower Roller	3. Torque gm. cm.
H	5	482	6800
H	4	383	6200
H	3	297	5600
L	5	238	5200
L	4	190	4900
L	3	144	4500
L	2	97	3900
L	1	49	2800

Conditions other than the above:-----

Density of ink-----1.1187

Wt. of sample-----2.1041

Lot II received Sept. 24, 1931.

H	5	480	6000
H	4	388	5500
H	3	295	4950
L	5	240	4600
L	4	192	4250
L	3	144	3800
L	2	98	3200
L	1	49	2400

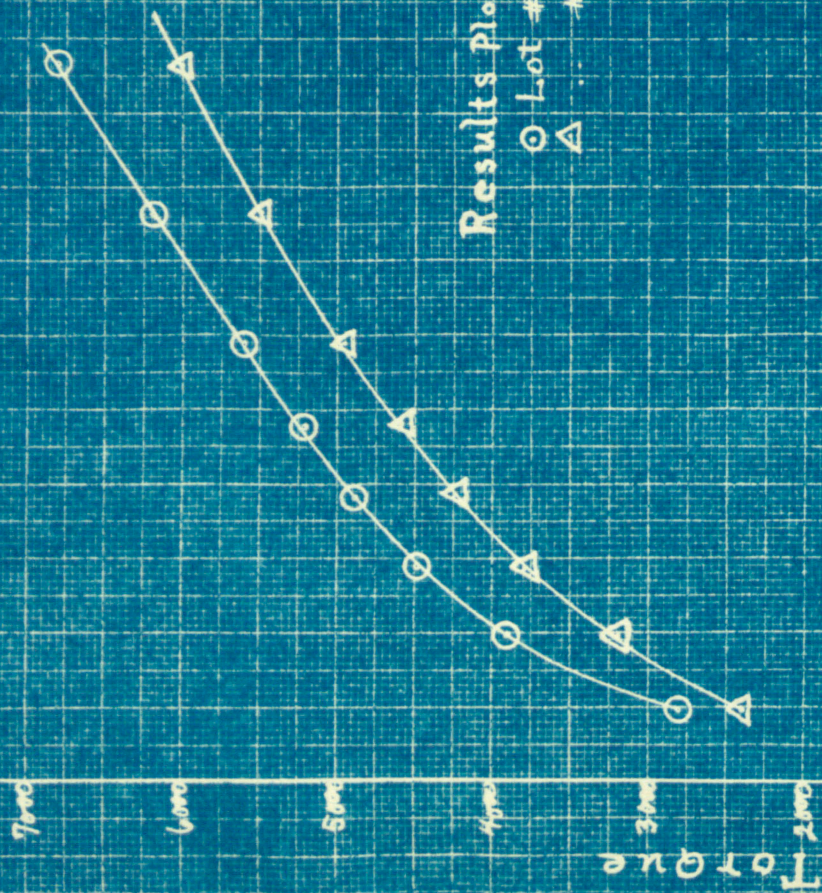


Figure 34.

Summary

Due to the fact that this work was a preliminary study in the measurement of the physical and chemical properties of lithographic ink, the samples of inks prepared for study represented simple composition. For the most part, therefore, these inks consisted of dispersions of hydrous aluminum oxide in varnishes of various viscosities. Inks of different consistencies were also prepared by varying the proportions of pigment and vehicle.

In order to make it possible to duplicate results, it was considered necessary to determine the physical and chemical properties of the linseed oil varnishes used as vehicles. The specific gravities, absolute viscosities, acid values, and refractive indices of the varnishes used were therefore determined.

A capillary type of extrusion plastometer was constructed and used to determine the effects of variation of temperature, capillary size, aging, moisture content, and concentration of pigment, on the consistencies of inks. This work indicated that this type of plastometer gave erroneous results, which necessitated the design and construction of a new type of instrument.

This new instrument was constructed in such a manner that inks could be tested under conditions analogous to those existing when an ink is being printed. In the preliminary

work with this instrument, tests were made on lithographic varnishes of known physical and chemical properties. In the case of inks the effects of variation of temperature, film thickness, concentration of pigment in vehicle, and a few reducing materials were studied. In addition, a number of commercial inks were tested.

It is unfortunate, that the time was insufficient to carry this research into further detail and to develop the theory related to this problem more completely. While the results are insufficient to allow many generalizations to be drawn, it is felt that some progress has been made in the desired direction.

Conclusion.

It was observed that the measurements made with the extrusion plastometer were in error when plug or partial-plug flow occurred, and that they were accurate only when perfect telescopic flow took place. Lithographic inks have a certain amount of internal structure, and when forced through a capillary some degree of plug flow always resulted. This was especially true in the case of inks which had high yield values. It was noted that the higher the yield value of the ink the more pronounced was the tendency toward plug flow, and the more like spaghetti the ink appeared after extrusion.

A long ink of low mobility and a short ink of greater mobility as determined by the finger measurements were tested by means of the plastometer, and the results just reversed. The long ink appeared to have greater mobility than the short ink. This was due to the fact that telescopic flow was taking place to a greater extent in the case of the long ink, while plug flow was taking place in the short ink. In the latter case, slip only takes place between a limited number of the outer-most imaginary concentric cylinders and the diameter from the capillary wall to which this slip extends, will depend upon the internal structure of the ink. In fact, the result is the same as if a smaller capillary was used.

The yield value gave information concerning the length of an ink, since a low yield value was characteristic of a

long ink, while a high yield value was indicative of a short ink. However, it was observed that the yield value was not a reliable criterion since it varied with time, previous working, and whether it was approached from the direction of increasing or decreasing pressure. In addition, this type of plastometer gave no information concerning tackiness. Apparently the pressure causing flow was not great enough to give a shearing stress comparable to the splitting of a thin film of ink at a high rate of shear.

It was noted in this study that an ink became more mobile and longer with an increase in temperature.

When true telescopic flow occurs, the yield value and mobility are independent of the capillary size. However, when a material exhibits plastic properties, this is no longer true. In such a case, the apparent mobility tends to increase, and the yield value tends to become smaller with increase in capillary size.

Another disadvantage of this type of instrument was that its operation was too time consuming. Nearly three hours was required to make a complete determination. It was realized, therefore, that such an instrument could never be used in the practical plant control of inks. For this purpose a test is required that can be made in 3 to 5 minutes.

These deficiencies made it necessary to design and construct another instrument called a "Tackometer", which was a form of a dynamometer. In testing inks with this instru-

ment, which measured a property closely related to tack, the torque readings were plotted against the speed at which a film of ink of known film thickness was split. Characteristic inks tended to give characteristic curves. Long, tacky inks gave a steep curve, while short, soft inks gave lower torque readings and hence flatter curves.

That this instrument did not tell the whole story was evidenced by the fact that a series of long inks gave a family of curves very similar to those obtained for a series of short inks. The instrument, therefore, was incapable of distinguishing satisfactorily between long and short inks.

It is felt, however, that further research will make possible the development of a scientific method of length determination, which, when used in conjunction with the tackometer, will surmount this difficulty.

It was noted that as the concentration of hydrous aluminum oxide was increased in a varnish of known viscosity, the tackiness increased. The mobility and length of an ink was observed to decrease with an increase in concentration of the pigment. This indicates that perhaps tackiness may be dependent upon some combination of mobility and length.

Although the Tackometer is still in the early experimental stages, it is felt that its use would furnish a better method of standardizing inks than the empirical finger methods now in use. This statement is supported by the study of inks obtained at different times from a reliable ink

company. The test can be made quickly, a minimum of 3 to 5 minutes, and a maximum of 30 minutes, being required. In addition, this instrument would give information that could be recorded in files, doing away with the keeping of samples, and prevent the drifting of standards due to aging.

Acknowledgement.

The author wishes to express his gratitude for the assistance and encouragement of Professor Robert F. Reed, who suggested this research and who, by his careful supervision and constructive criticism, has directed this investigation.

The author also wishes to acknowledge the very valuable assistance given by Mr. Paul W. Dorst and Mr. Edward T. Johnson.