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Size Tests Applicable to Writing Surface versus Aqueous Inks

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SIZE TESTS
APPLICABLE TO WRITING SURFACE
VERSUS AQUEOUS INKS

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requirements for graduation, the Pulp and
Paper Technology Curriculm at the
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Kalamazoo, Michigan

Md. Mozammel Haque
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ACKNOWLEDGEMENT

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TABLE OF CONTENTS

Literature Survey

Introduction

Some paper, because of their use requirements are required to be porous and absorbent to liquids, particularly water. Examples of these papers are paper towels, blotters and filter paper. Most papers, however, are required to be resistant to the passage of acquous liquids or vapor. Writing papers, moisture resistant bags, waxed paper and many other classes of paper too numerous to mention fall into the latter groups of papers.

The required degree of resistance to the penetration of aqueous liquids or vapors is brought about through the process of sizing. Sizing may be defined as the addition of materials to the furnish for paper or board in such a manner that these materials increase the resistance of the sheet to penetration by liquids or vapors. In order to make paper less absorbent it is necessary to more or less coat the individual fibers with materials which are water resistant. It is possible to accomplish sizing with several different materials which are commonly used. Sizing may be classified either as "Beater" or "Surface" sizing.

Effect of Sizing on Paper

Beater sizing has been defined by John Turbyne (6) as "the addition of the sizing materials before the sheet is formed. In this type of addition the sizing materials are usually in colloidal suspension when added and then are later precipitated on fibers." Tub sizing may be defined as "the addition of the sizing materials to the surface of the sheet after the sheet has been formed, either before or after the sheet has been dried. In this case the sizing material is of an adhesive nature in order that it will not be easily removed from the fiber when the surface of the sheet is rubbed or erased."

It has been shown by Ralph W. Kumler (6) that "cellulose fibers are naturally hydrophilic in nature and in the absence of chemical treatment readily absorb water. Beater sizing consists of the attachment of hydrophobic substances to the individual fibers so that when the sheet has been formed and dried a certain degree of reduction in the rate of water absorption is established. The pores in the sheet are not appreciably filled and there is no reason to believe that the fibers are completely coated. The techniques of microscopy have not yet advanced to such a point that we can see the distribution of the size in the papers, but the fact that most highly sized papers do absorb water lends credence to the supposition that the coverage with sizing materials is only partial. The principle has been illustrated by treating a wire screen with paraffin wax either by dipping or spraying. Although air or steam will pass through readily, liquid water will not do so except under pressure (6).

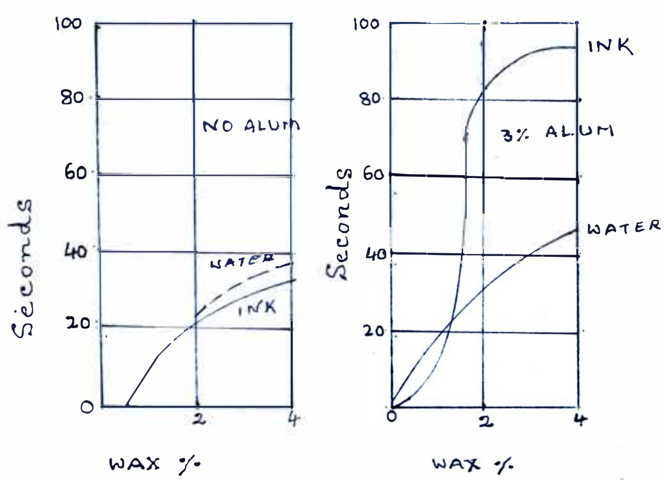
Physical Aspects of Paper Sizing

It has been demonstrated by William Bond Wheelwright (10) that when paper is made without the addition of sizing, it is more or less absorbent, depending upon the character of the beating. In the case of blotting paper the beating is done with sharp beater knives, causing a gelatinous condition by hydration, which serves as an adhesive agent helping the fibers to cling together and makes them more resistant to grease and moisture. Sizing is not required to hold fibers together but is necessary to retard the penetration of water or spreading of writing fluid (which has a water vehicle) to prevent fuzzing of the surface fibers and to impart the paper degree of stiffness (10).

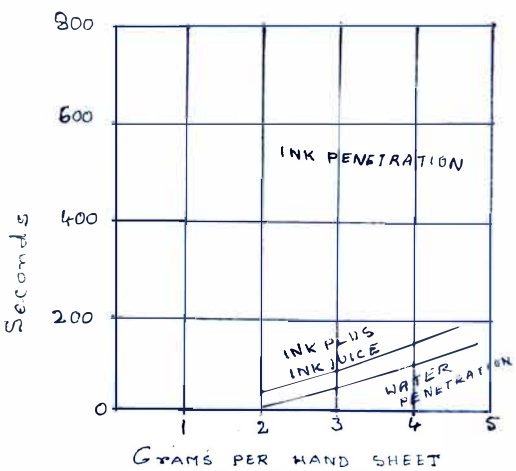
It has been shown by R. N. Cobb (9) that, in papermakers terms the slower the rate of penetration, the harder the degree of sizing. Sizing treatments are applied internally by precipitation on the fibers in the beater or by surface treatments of the web paper. Sizing is generally supposed to decrease the rate of change of moisture when paper is brought into press room, but no accurate study of the problem has ever been made. However, paper is sized to close the pores and prevent the feathering of aqueous ink, either on the first lettering or after erasing; or to increase the surface strength and resistance to picking of fibers in printing; or to make the surface smoother and reduce the absorption of printing ink. Surface sizing influences writing and printing qualities, and to some extent the coating and laminating properties imparted may differ from those given by internal sizing. Surface sizing also differs from internal sizing (9) in that a drop of liquid tends to penetrate down into empty capillaries more readily than it tends to spread sideways over the surface of the sheet.

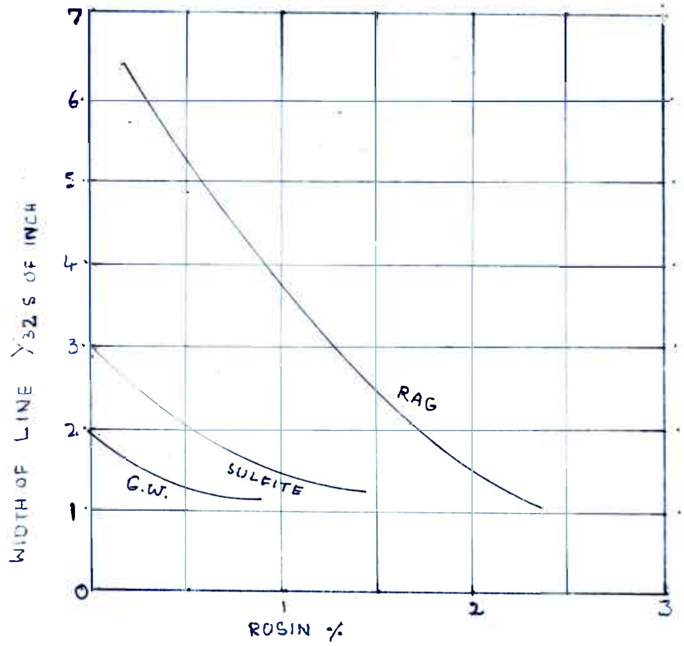
Some Properties of Ink

It has been advocated by William Wilson (11) that the properties imparted to a piece of paper by engine sizing should be analyzed and he has given an explanation of the relationship between water penetration, ink resistance, ink spreading, and time of ink drying. Water penetration depends largely on the type of pulp and amount of size, where as, ink sizing is a factor of the amount of alum and its ability to coagulate the dye in the ink (11). Most of the sizing tests used in the paper industry can be divided into two classes. First, those which determine the average rate at which a liquid penetrates the sheet, and second, those which determine the average rate at which a dye, suspended in the liquid penetrates the sheet. The ink penetration test presumably measures the amount of ink spreading likely to occur when the sheet is written upon. If the ink is poured on the centre of a filter paper there is some light indication of a separation of the dye particles and the liquid as the stain travels to the outside of the sheet. Without alum there would be no coagulating effect from the pulp and therefore the ink and water penetration tests should be the same (11). If the alum is added to the furnish one should obtain slightly higher water penetration tests as indicated by Redd's work (11).

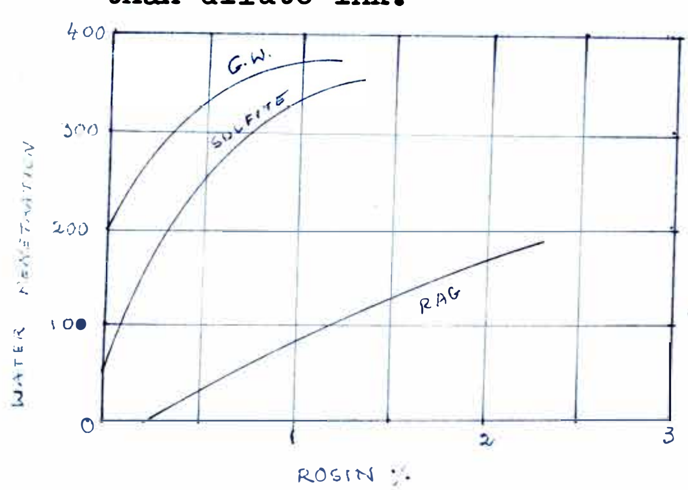


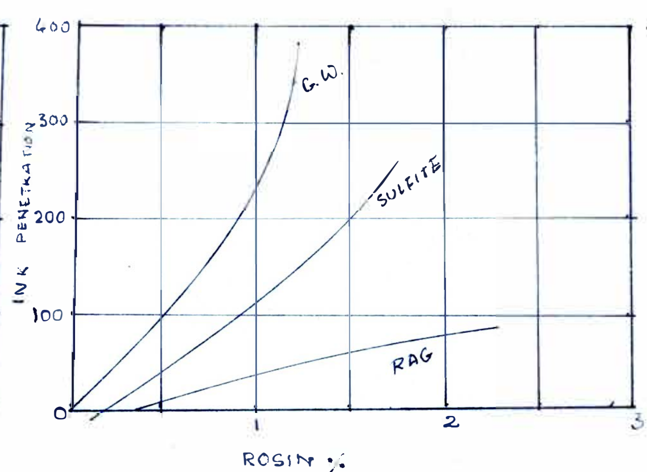
With the alum the coagulating power of the pulp has been affected and the ink penetration tests should be much higher than the water penetration tests (11).





It has been further shown by William Wilson (11) that the above experiments prove that the ink liquids travels at a faster rate than the ink dye. After penetrations were run with water ink, and ink juice with no dye in it, it was found that concentrated ink went through the sheet 40% faster than regular ink, which in turn was 150% faster than dilute ink.





However, these data indicate why people prefer to write on rag paper. One can get any desired resistance to ink spreading without at the same time building up a water resistance which makes writing difficult or unpleasant.

In one article, written by Smith (8) "It is well known that various published and accepted tests for sizing in which permeability to water is measured do not run parallel with tests made with writing ink; the principle objection to insufficient sizing being feathering of the ink. There is a number of tests more or less in general use such as flotation test drop, and actual application of an ink with a pen that indicate the nature of sizing but are not necessarily measures of feathering. They are reported as sufficient and insufficient sizing and are not numerical. Grading is practical to observe deterioration over a period of time or for other reasons. Moreover, there is no indication of the behavior of the paper with other inks".

At one time all writing inks contained gum arabic and generally a preservative of some sort and only a very poor degree of sizing was indicated by the simple and most universal test, application of an ink to paper with a pen. The development and use of fountain pens required a reduction in the amount of gum arabic because it clogged the feeding mechanism by drying, so that the gum has been decreased gradually until now very few writing inks contain this material.

The continued use of fountain pens and the desire to have them start immediately introduced surface active compounds and hygroscopic agents into the formulas. Smith (8) then decided to make three standard inks that would approximate the behavior of those active in feathering, along with an ink made by the formula given in TAPPI T-431 m. A more or less empirical formula was adopted and the active material made in two strengths. These are matched to the commercial inks in their feathering characteristics with a standard grade of paper. Generally the results are independent of the pen point that is used, although a ball pointed pen and sharp points give false indication at times. Atmospheric conditions do have an effect on the final results (8).

Degree of sizing on Writing Paper

It has been demonstrated by Schur (6) that "a test is described for the determination of the effectiveness of the sizing in writing paper. It has the advantage of being objective and direct. The method is based upon the measurement of the surface spread of ink lines drawn under closely reproducible conditions. The instrument employed for drawing the lines and its operation are described, and a standard ink is discussed. Typical research data obtained with the aid of the test presented". The ink used is a 1% solution of methylene blue in 0.5% phosphoric acid.

Average Maximum Spread, %.	Degree of Sizing.
10-15	excellent
15-20	good
20-25	fair
25-30	borderline
30-	poor

The effect of relative humidity is shown in the following values:

Relative Humidity at 70°F, %.	Average Maximum Spread, %.
20	29
34	46
47	57
65	63
85	56

"The problem of measuring the effectiveness of sizing in writing paper is more complicated than might be thought, although ordinary pen and ink tests may furnish some idea of ink fastness. Observers are apt to vary in their judgement of results to a disconcerting extent, particularly if the paper is differently sized. Lack of agreement may be laid to a number of variables, for example: the type of pen point used, whether sharp, stub, or ball: the nature of the pen stroke, whether bold or light: the quantity of ink on pen: and the status of the observer."

"An excellent bibliography of sizing tests together with abstract has recently been published by the Institute of Paper Chemistry (Wisconsin) (165 Pt.1, 165 P # 2, Pt. # 3, 165 Sn II 1945 (3). In it will be found methods involving measurements of the rate of penetration of ink through the sheet, also procedures employing a dry indicator sprinkled upon or painted on one side of the paper sensitive to some type of the electrolyte applied to the other side; and similar tests involving the use of a fluorescent dye as indicator. Still another method uses as its basis the rate of pick up or absorption of water." However, "they fail to detect differences in the ink resistance of the two sides of the sheet and in many instances are difficult if not impossible to interpret, particularly when complicating variations in sheet thickness are encountered in the comparison of different samples of paper." "Although the draftsman pen would be an improvement over the common pen, it is far from satisfactory, for the spread of the ink may be influenced markedly by the head of the ink in the pen, the pressure on the pen, width of the pen, tilt and sharpness of the pen, the angle between the line being drawn and the plane through the slot in the pen, and the velocity with which the line is drawn. These variables have been eliminated to a negligible extent in a rotary pen of special design."

"The width of the pen slot is ~~conventionally~~ conveniently determined with the aid of a microscope set to magnify about 100 diameters and provided with an occular calibrated micrometer." Work at the Bureau of Standards indicated (1,8) that the curl test and the dry indicator test offered the most accurate methods for determinating the internal sizing of a paper. Work was carried out with these tests using the Carson curl sizing tester or the penescope. The curl test made with the Carson curl sizing tester seems to give the most uniform data.

It has been shown by J. E. Alexander (2) that the Valley size tester is a modification of the method by Okrell; the theory is that the conductivity of the paper for electric current increases with the gradual permeation and the final saturation of the paper by a solution of an electrolyte. A curve is given showing the increase in the results of the Valley size test with the increase in basis weight of a hard sized sheet, the furnish being 80% sulfite and 20% mechanical pulp. The test can not be used for comparing papers of different grades.

It has been shown by Jenckel and Culemeyer (5) that on an adequately sized writing paper, ink should not spread, and should never form bead-like-driplets. It must adhere to the paper surface. This bead-like formation has not been considered in the past, because it is very seldom referred to as a sizing agent. Unsized and sized sheets are wetted completely with water and ink. The capillary rise in sized paper is far less than with unsized sheets.

It has been demonstrated by Brech and Liebert (12) that attempts were made to detect the wear on the surface of paper by various writing pressures and amounts of ink deposited by various styles of fountain nibs, with the object of effecting sizing economics. The results, presented graphically, show the relation between ink consumption and pen stroke, and the distribution of ink exerted by individuals among a group of penwomen and penmen. The amount of ink deposited in Mg./Sq.Cm. by a certain type of pen nib with a stroke of unit width is a measure of the strain placed on the paper sheet. The harder and broader nibs deposited less ink than the softer and narrower ones for the same unit width and caused less wear and tear of the sheet surface.

A Capillary System of Paper Fibers

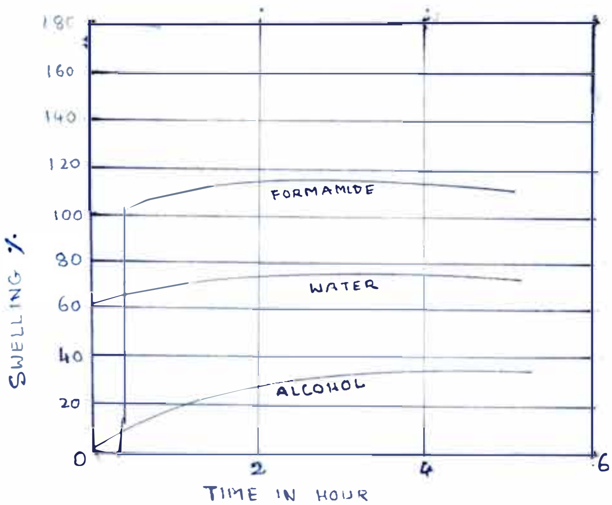
It has been shown by Foote (4) that the effective fine diameter of the capillary system contained in a sheet of paper is important in studying the penetration of liquids into a sheet. A measure of the pore diameter dan be obtained by means of the Lucas equation; $D=4nk/W$, where D is pore diameter, n is viscosity of the liquid, W is surface tension of the liquid and k is constant.

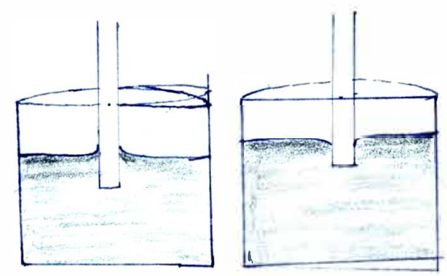
The value of K can be determined by studying the rate of capillary rise of a liquid in a strip of paper. This equation does not take into consideration the swelling action of the liquid and the fiber. By application of these factors the accuracy of the method should be improved. Two strongly swelling liquids (formamide and water) and two which dissolved rosin readily (alcohol and benzene) were used. The second two were used so that determinations on rosin sized sheets could be made. The quantitative swelling data for water, formamide and alcohol were taken from the work of Kress and Bialkowsky.

// To measure the angle of contact a micro-projection method was developed in which individual fibers were dipped into a liquid surface. It was found that in the application of the swelling and contact angle data the results obtained by the Lucas equation could be rationalized. The effect of the swelling and the contact angle was clearly shown. Alcohol appeared to give the most correct value. The angle of contact is zero and the short time required to complete a determination reduces the swelling effedt to a negligible factor. Alcohol can be used on rosin-sized and non-rosin-sized samples with equal success. Some very interesting facts were found in the contact angle studies.

Quite extensive data indicated that alcohol always forms a zero angle of contact. This condition also prevails on more limited data for formamide and benzene. Water, on the other hand, gave values greater than zero. The angle is increased by impurities in the stock, rosin sizing and certain surface sizing materials.

An increase in the TAPPI size test is concomitant with an increase in the angle of contact."





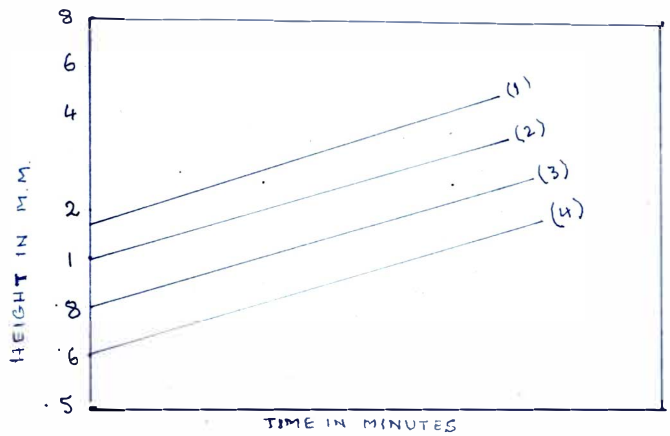
CONTACT ANGLE FOR WETTING LIQUID

CONTACT ANGLE FOR NON-WETTING LIQUID.

The angle of contact formed between the fiber and water varies from point to point along the fiber, and the average value varies with the type of fiber. The angle of contact is decreased by bleaching and purification. The TAPPI size test is closely related to the contact angle. With hand sized fibers, the contact angle appears to be an additive effect of the original angle of contact of the fiber and induced by the rosin size. Starch surface sizing and glue set with formaldehyde increases the angle of contact formed by alcohol, benzene and formamide. Pore diameters indicated for the various liquids can be corrected by means of swelling and contact angle data. Values presumably close to the correct value of the effective pore diameter can be obtained by the use of alcohol.

Surface sizing materials decrease the size of the pore. Pore diameters are larger in the machine than across the machine direction.

Liquid.	Height-width.
Alcohol	2.31
Benzene	2.30
Formamide	2.26



Log/log relation between height of capillary rise and time. 100% sulfite sheet, rosin size extracted, not top sized; strips cut across the machine direction.
(1) Benzene (2) Alcohol (3) Water (4) Formamide.

To study the rate of capillary-rise, strips about 15 mm in width were dipped into various liquids and the rate of capillary ascension was followed by means of a cathometer. To assure uniform conditions, all the tests were carried out in a constant temperature room, and all the samples were humidified at least 24 hours before using. The temperature of the room was controlled at 70°F and the samples were conditioned at 65% relative humidity. The materials consisted of two samples of No. 1 sulfite bond.

The first sample was taken from a paper machine immediately before the sheet was to enter the surface sizing tub, and the second was taken from the finished paper. In order to insure that the fundamental characteristies of the two, samples were taken from adjacent positions in the web. Top sizing of the second sample was carried out by passing the sheet through a tub of 100% gum (modified starch) at a consistency of about 4 degree Be.. The temperature of the tub was maintained at 120°F.

Abstract... The relation of feathering of inks on the many sized papers has been of paramount importance to the Paper industrialist and printer since the invention of paper.

The term " Feathering" of ink refers to the spreading of the ink line as it is drawn on the paper, due to the absorption of the ink by thirsty paper fibers. The more thirsty the fibers, the more the line will spread and blur. This can be remedied in two ways; (1) By decreasing the pH of ink or, (2) increasing the size content. Inks of low pH don't spread or feather to a great extent, and likewise papers of high size content prevent extensive and noticeable feathering. High size content refers to addition of Rosin to the paper, which makes fibers less absorbent.

From these facts the paper manufacturers and printers can coordinate their knowledge in producing a printed page which is clear, yet use less ink. This is of unparalled value to the consumers who buy millions of printed pages every day. This knowledge thus gained will be of great value to paper industrialist, printer and consumer. It will mean a higher quality product at a lower cost to all.

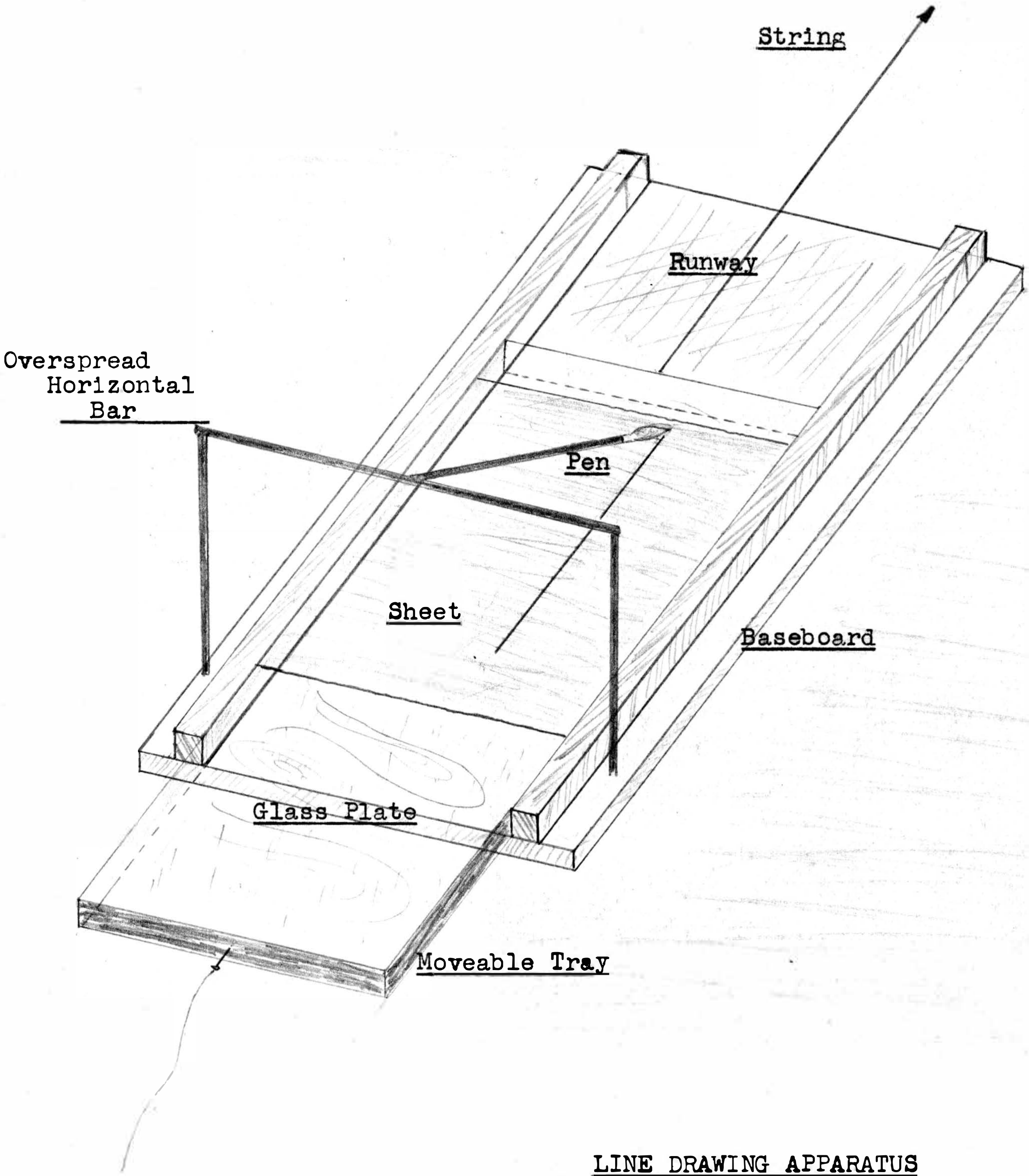
Summary... The purpose of the experiment was to determine the surface feathering of different inks on several sized papers. The Hawthorne Paper Company of Kalamazoo, Michigan was of great assistance, giving papers and data to work with. Without their kindness and cooperation, the work could not have been executed.

The papers were classified into six major groups according to size content in the following way:

I.	50% Rag Book Paper	1.80%	Rosin Size
II.	50% Rag Index	3.50%	" "
III.	25% Rag Bond	1.70%	" "
IV.	25% Rag Ledger	2.00%	" "
V.	Special Paper	1.90%	" "
VI.	Water Resistant	2.10%	" "

Six inks were used. Four were commercial inks, the fifth was Tappi Standard ink, sixth was Methylene Blue ink. Methylene Blue ink was made by dissolving 2 grams of Methylene Blue dye in 1,000 cc distilled water. The ink was then filtered before using. PH was determined by using glass electrode. Following inks were used:

I.	Carter's ink (blue)	2.1 pH
II.	Morriset (blue black)	3.0 pH
III.	Parker Super Chrome (Black)	12.2 pH
IV.	Carter's Jewel ink (Black)	8.6 pH
V.	TAPPI Standard ink	3.4 pH
VI.	Methylene Blue ink	6.6 pH



LINE DRAWING APPARATUS

Description of apparatus... The line drawing mechanism consists of four main parts: baseboard, overspread horizontal bar, moveable tray, and electric motor. The baseboard, which is stationary, serves both as a mounting board, and as a runway for the moveable tray. The runway is made by nailing a narrow strip of wood on each side of the baseboard. These strips are placed in ½", allowing for a lip which is used for another purpose. Then the runway is lubricated with soap to prevent the moveable tray from sticking. This tray, in which a glass plate is placed for use as a drawing surface, is pulled along the runway by means of a string winding around the wheel of an electric motor as it turns.

The overspread horizontal rod is supported by two vertical rods extending 12" above the lip of the baseboard in which they are imbeded. The purpose of the overspread horizontal rod is to hold the pen in a fixed position above the paper. Lastly, the pen is fastened to the rod at a specified angle to the moveable tray, drawing a line on the paper as the tray moves underneath it.

Procedure... The sheet being tested was placed on the glass plate in the movable tray and was fastened down by a wood strip. Then the pen was lowered onto the paper at a fixed angle and held there by a fixed weight applied to the pen. The pen used was a draftsmen ruling pen. It held a constant volume of ink, the flow of which was controlled by the fixed opening of the nibs. It was the sheet alone that moved along on the plate and tray, while the pen remained in the same position, causing a line to be drawn. A glass plate was used in the tray because of its smoothness which aided in the drawing of a uniform line. After each application, the nibs were thoroughly cleaned.

In order that all sheets should have a constant moisture content, they were kept in a humidity room. The only time they were taken out was for drawing lines and taking measurements.

To measure the degree of feathering, a calibrated microscope was used. Both the width of the opening of the nibs and the width for line measurement were made. It was the difference between the width of the nib opening and width of the line, as measured, which determined the feathering.

Results... The following information indicates the featherings which were detected with each ink as applied to the various papers:

Papers	Feathering of Inks in mm.				
	I	II	III	IV	VI
50% Rag Book	.0176	.0136	.0425	.0341	.0236
50% Rag Index	.0150	.0163	.0468	.0327	.0264
25% Rag Bond	.0183	.0159	.0443	.0357	.0260
25% Rag Ledger	.0157	.0156	.0575	.0360	.0257
Special	.0171	.0187	.0433	.0348	.0286
Water Resistant	.0151	.0163	.0458	.0360	.0264

It has been indicated by the experiment that Carter's ink No1 of 2.1 pH showed no feathering on 50% Rag Index paper with Rosin size of 3.5%. TAPPI Standard ink was tried but failed to produce satisfactory results. However, Methylene Blue ink was applied with different ranges of pH, and as has been indicated, with an increase of pH an increase of feathering resulted. Likewise, with an increase in Rosin content, a corresponding decrease of feathering was produced. Graphs have been drawn showing feathering against pH of inks tested on different sized papers. In addition, photographs of the lines have been taken to show the results from the experiment.

Results... The following information applies to both the graphs and the photographs:

Figure I shows the feathering of ink on 50% Rag Book Paper, sized 1.80%.

Figure 11 shows the feathering of ink on 50% Rag Index, sized 3.50%.

Figure 111 shows the feathering of ink on 25% Rag Ledger, sized 2.0%.

Figure 1V shows the feathering of ink on 25% Rag Bond, sized 1.70%.

Figure V shows the feathering of ink on Water Resistant Paper, sized 2.1%.

Figure Vl shows the feathering of ink on Special Paper, sized 1.90%.

Conclusion... It has been detected that the various commercial inks show more feathering with an increase at their pH. Conversely, the feathering decreases upon addition at Rosin size to paper.

Methylene Blue ink exhibited the same tendencies as other inks used in this experimentation.

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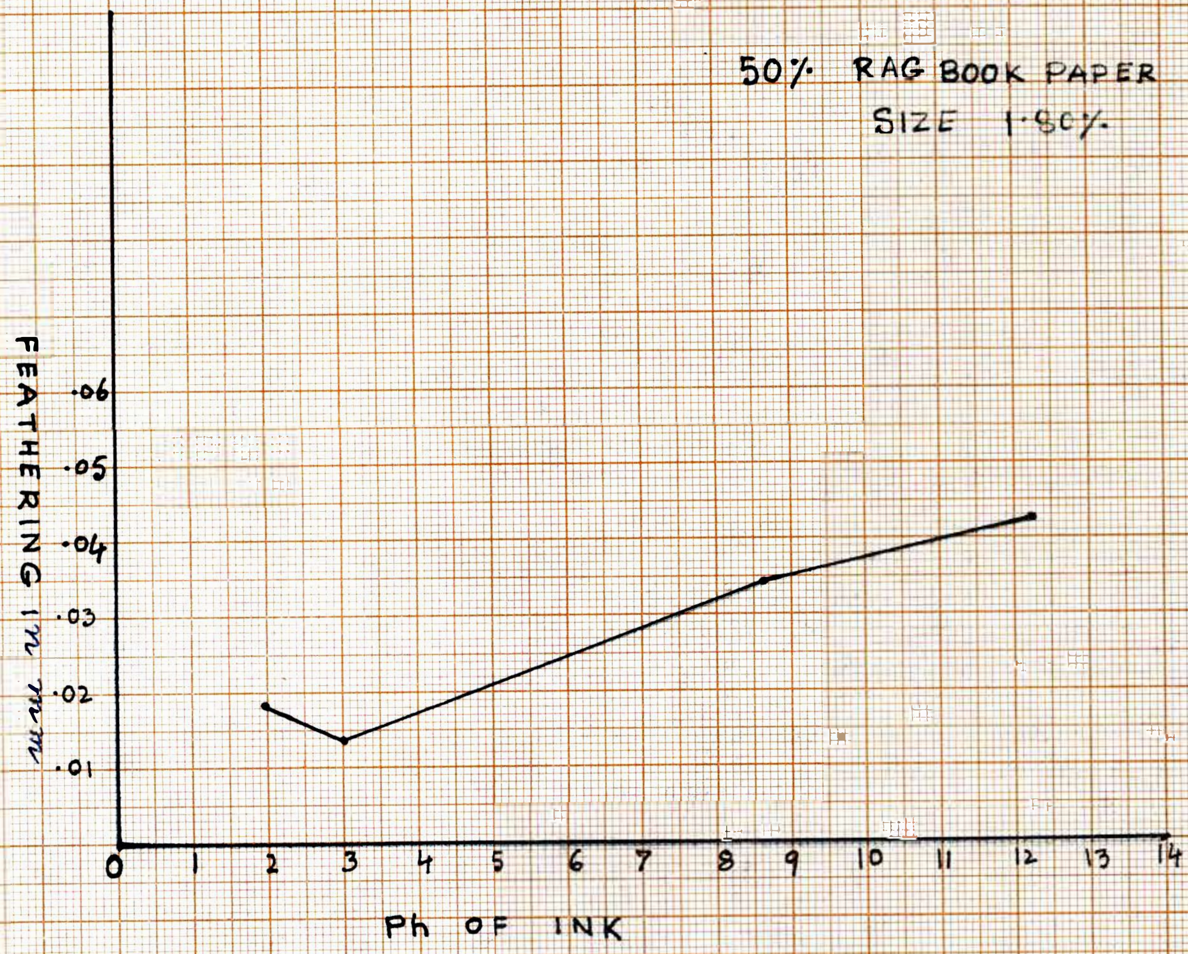
I


50% RAG BOOK PAPER
SIZE 1·80%
FEATHERING in mm
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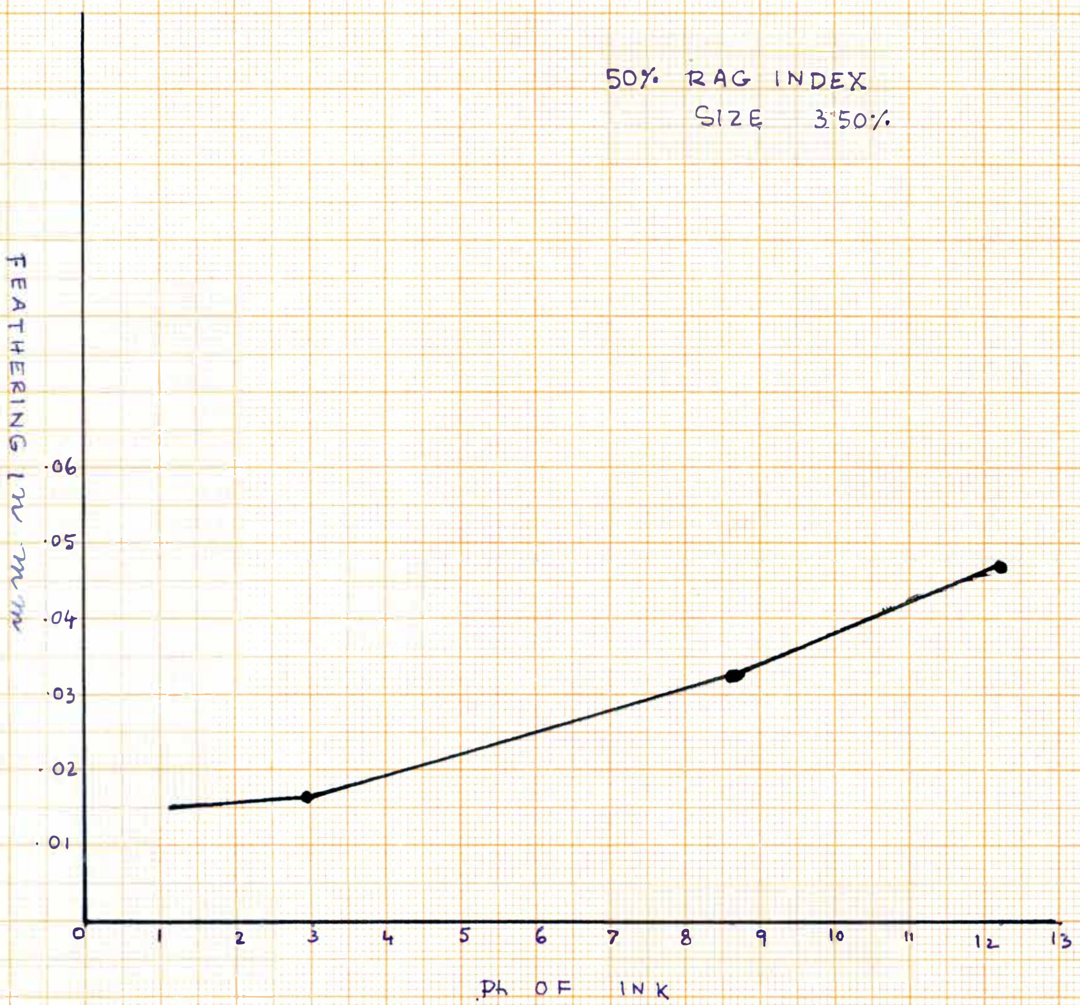
Ph OF INK

II



50% RAG INDEX
SIZE 3.50%
FEATHERING IN MM
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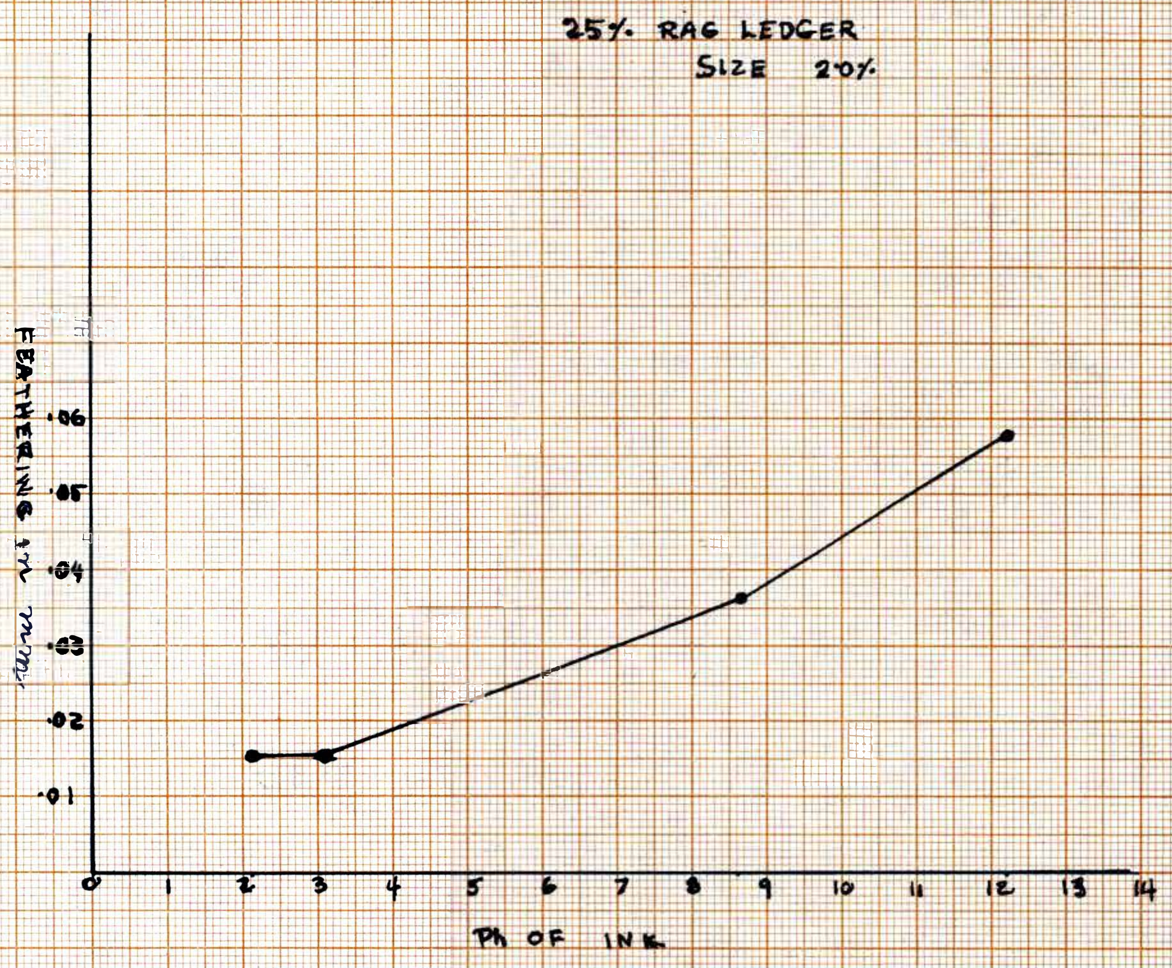
Ph OF INK

III


25% RAG LEDGER
SIZE 20%
FEATHERING in mm
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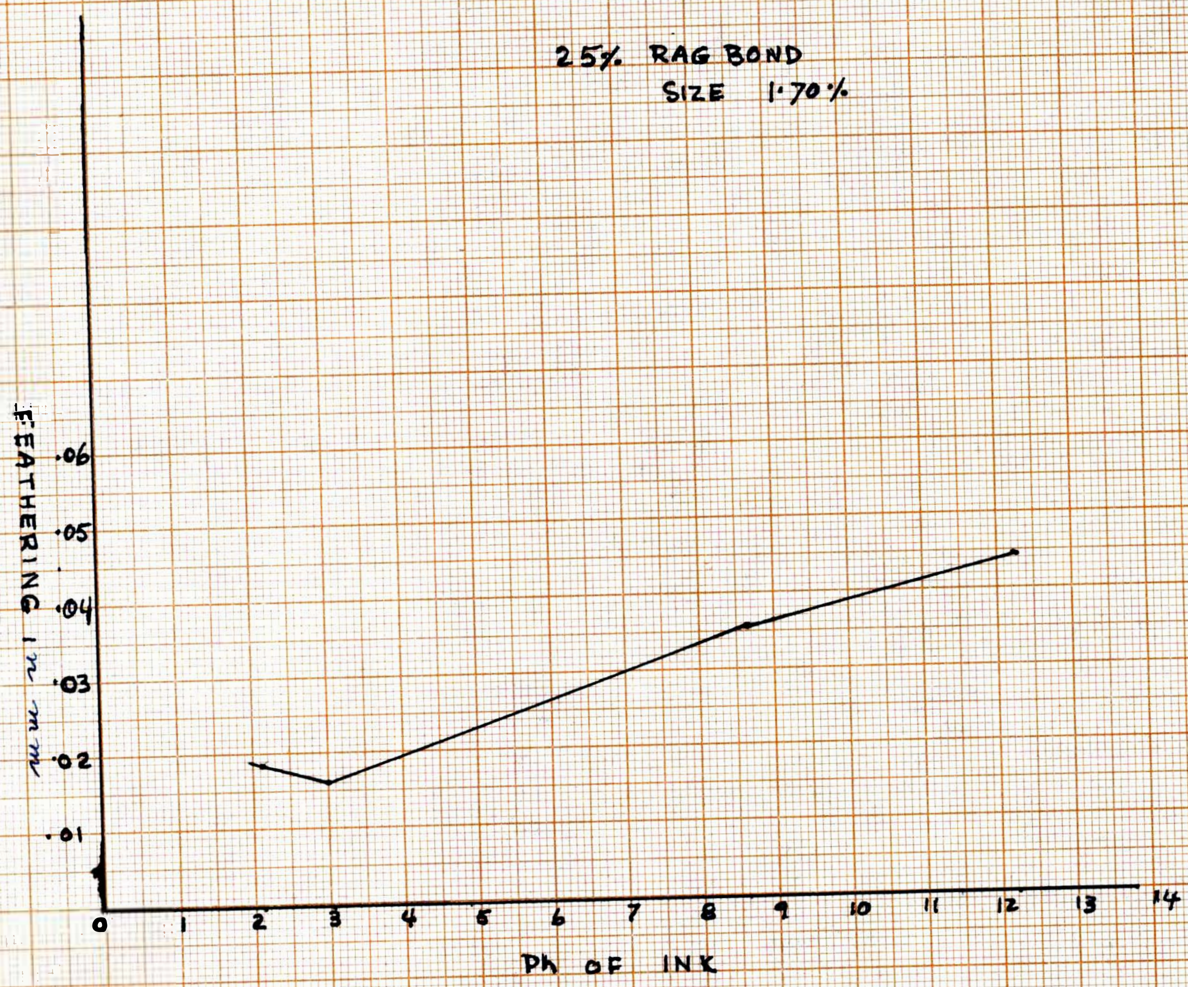
Ph OF INK

IV


25% RAG BOND
SIZE 1·70%
FEATHERING in mm
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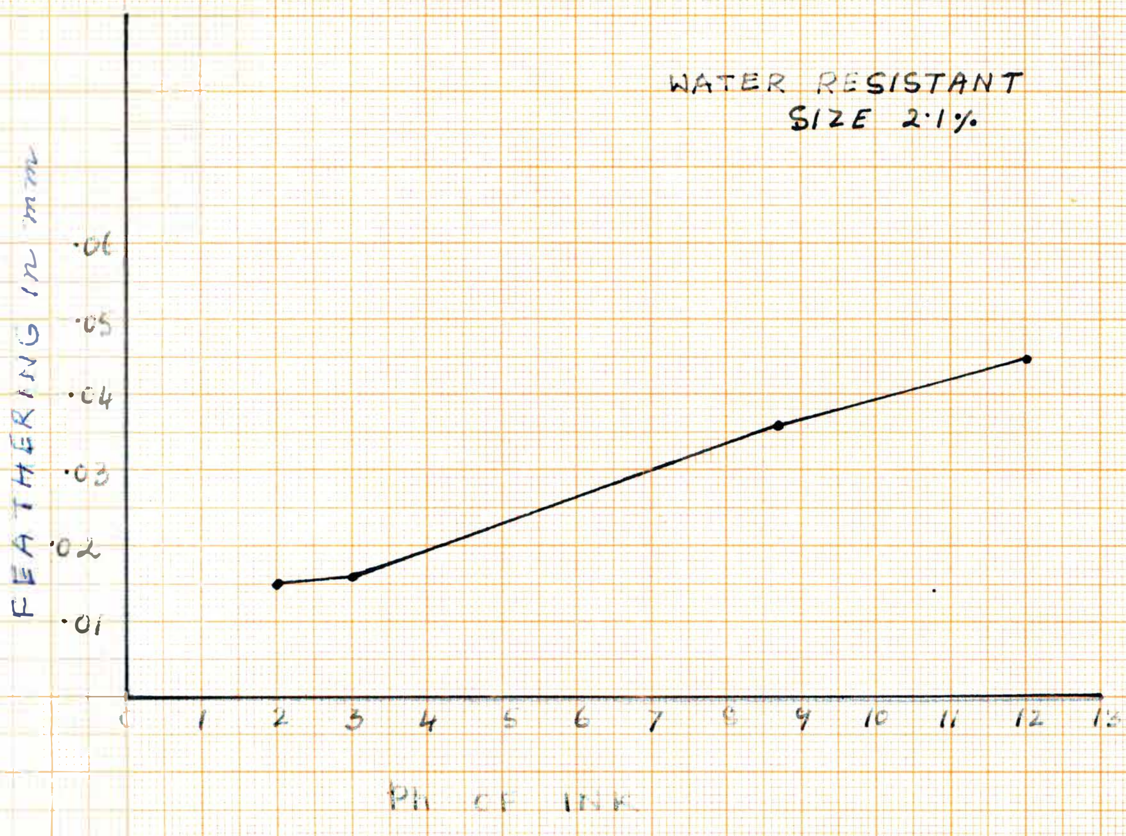
Ph OF INK

29

V


WATER RESISTANT
SIZE 2·1%
FEATHERING IN mm
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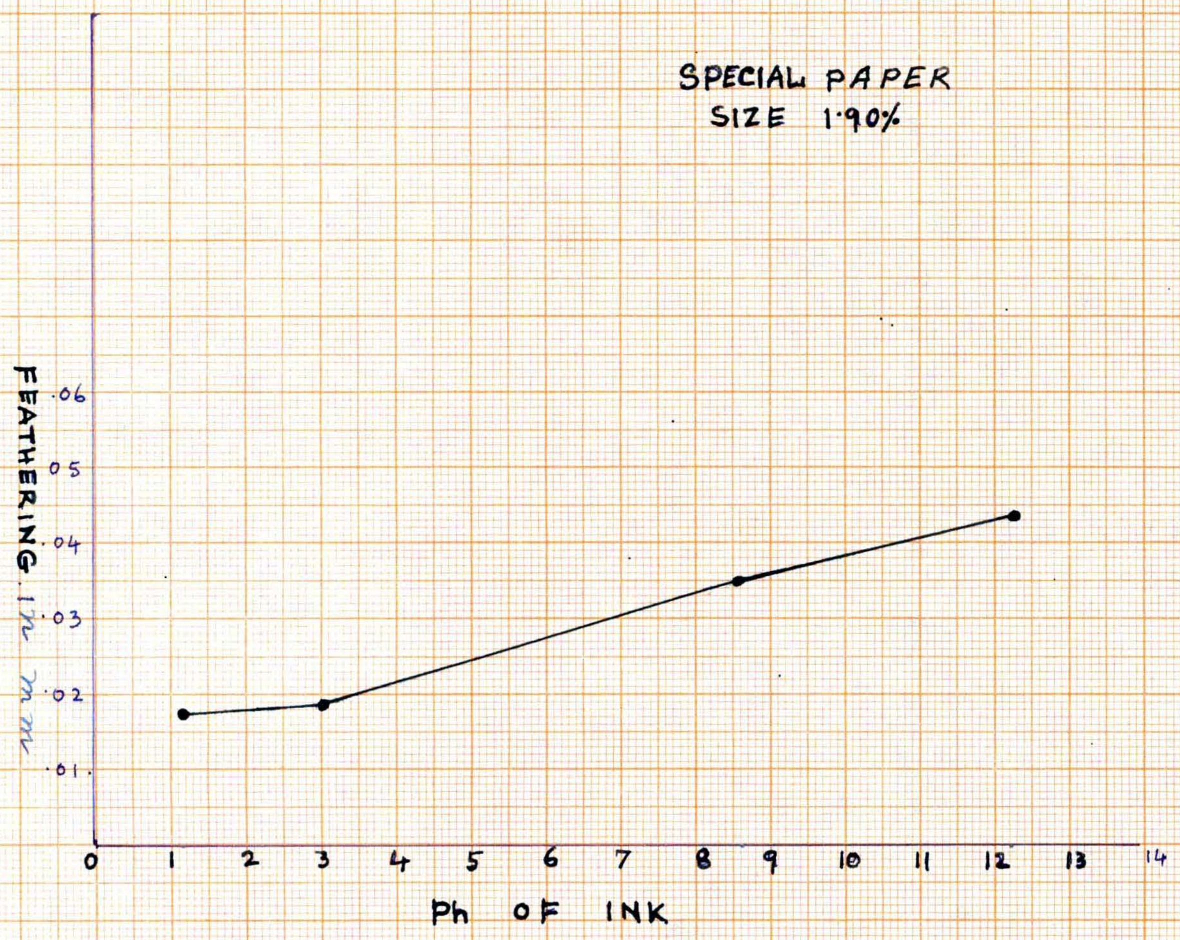
Ph OF INK

VI


SPECIAL PAPER
SIZE 1·90%
FEATHERING in mm
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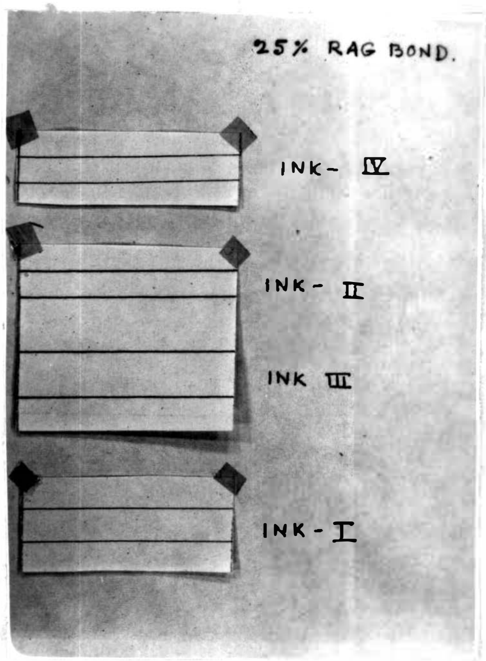
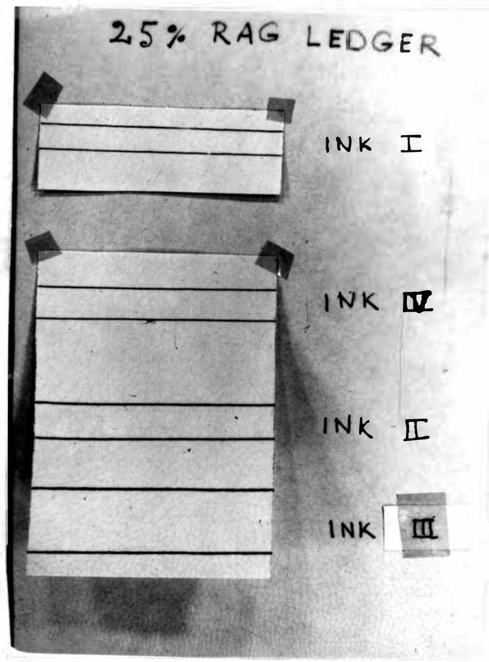
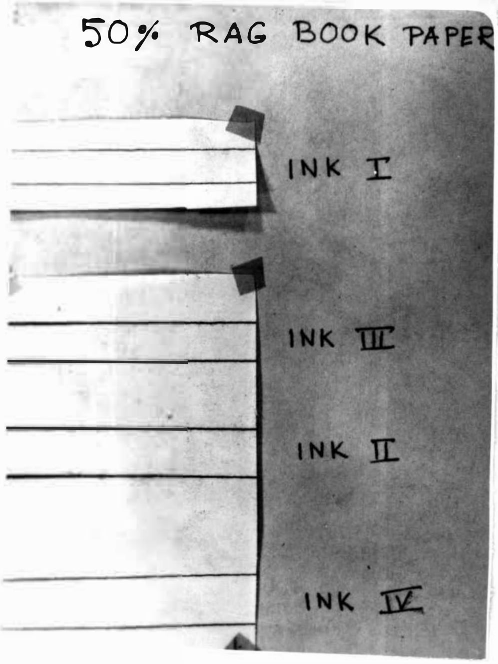
Ph OF INK



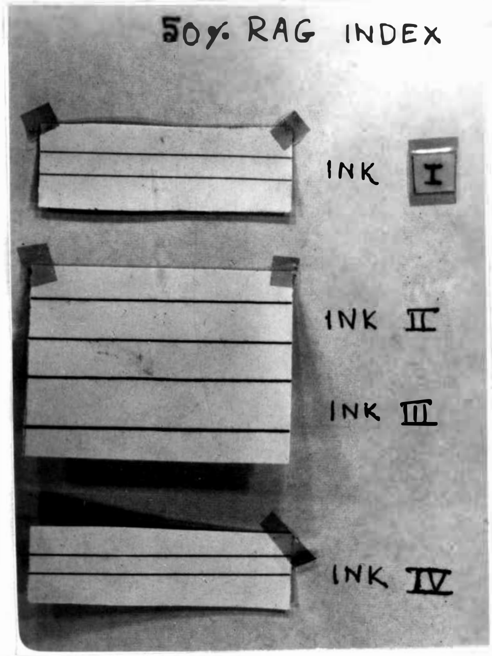
25% Rag Bond Paper.
Size 1.70%.



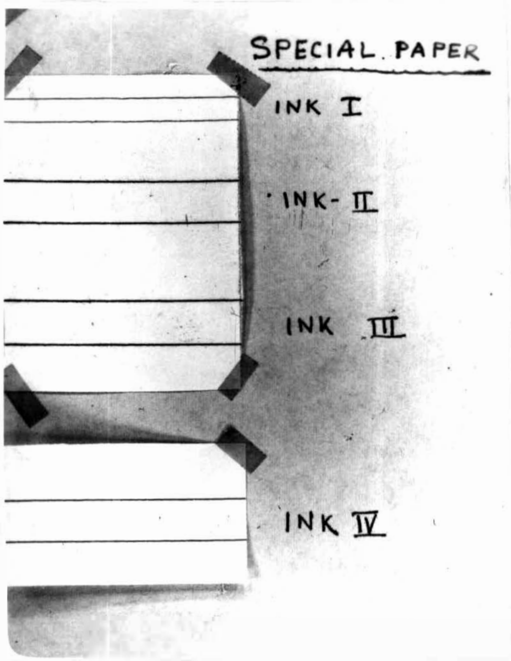
25% Rag Ledger.
Size 2.0%.



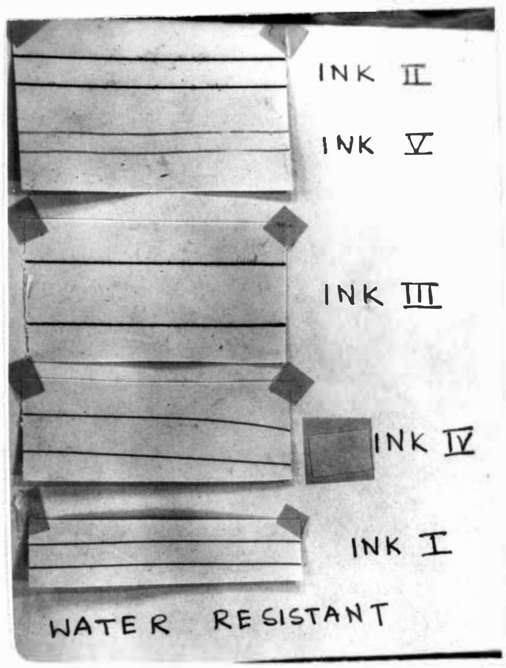
50% Rag Book Paper.
Size 1.80%.



50% Rag Index.
Size 3.50%.



Special Paper.
Size 1.90%.



Water Resistant Paper.
Size 2.1%.

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