

**RESEARCH IN SIZING ASPECTS OF THE
PAPER MAKING PROCESS**

**A thesis presented to the
Ahmadu Bello University in partial fulfilment
of the requirements for the Degree of**

M.Sc. CHEMISTRY (PROCESS).

By

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THIS THESIS HAS BEEN

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DEDICATION

To my parents

(iii)

A C K N O W L E D G M E N T S

My sincere thanks go to Professor A. R. Mathieson (Head of the Chemistry Department and Deputy Vice-Chancellor). To me he has this unique ability to understand and solve student problems. With this characteristic he ensures that students under him get the best out of their stay in the Department.

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TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS	vi
ABSTRACT	vii
CHAPTER I INTRODUCTION	1
II MATERIALS AND EXPERIMENTALS METHODS	17
III RESULTS	51
IV DISCUSSION	72
V CONCLUSION	84
REFERENCES CITED	87

List of Illustrations

<u>Figure</u>		<u>Page</u>
1	Hydrogen bondings in paper	2
2	Typical rosin acid structures	5
3	The paper machine system	23
4	Sketch of a sheet Former	24
5	Arrangement for Preparing Hand sheets ..	25
6	UV-absorption of rosin soap (In aqueous solutions without pulp)	33
7	UV-absorption of rosin soap in backwater	34
8, 9	UV-absorption of rosin in $CHCl_3$	36
10	Observed and calculated rosin in sheet at various pH values	39
11	Imported rosin calibration curve	42
12	Local rosin calibration curve	43
13	Aluminium calibration curve	47
14	Rosin in backwater with varying pH values	58
15	Total aluminium in backwater with varying pH	59
16	Aluminium in sheet with varying pH	60
17	Average sizing values with varying pH ..	61
18	Rosin in backwater with various rosin concentrations	63
19	Aluminium in backwater with various rosin concentrations	64
20	Aluminium in sheet with various rosin concentrations	65
21	Average sizing values with various rosin concentrations	66
22	Rosin in backwater with various aluminium concentrations	68
23	Aluminium in backwater with various aluminium concentrations	69
24	Aluminium in sheet with various aluminium concentrations	70
25	Average sizing values with various aluminium concentrations	71

A B S T R A C T

To minimise water absorbancy in paper (writing papers), the highly hydrophobic rosin is added. Optimum conditions for effective use have been studied by estimating the water penetrating rates of treated paper.

As a deviation from this general method we estimated the retention of the paper additives used in sizing under different conditions. The residual additives in backwater (pulp filterates) were estimated also. These quantities should be closely related to sizing values (penetration rates).

In our work the following were observed:-

(1) Optimum sizing with rosin is observed within a pH range of 4-4.5.

(2) Sizing values increased with rosin addition to a maximum value after which little increase is observed for further rosin addition.

(3) Sizing values increased with aluminium (alum) addition in a similar way as with rosin addition.

All these observations are in agreement with past works done to find optimum sizing conditions by evaluating the aqueous liquid penetration rates.

In this work also we tried to find out whether production of rosin locally in Nigeria is possible. Our conclusion is that Nigeria has all the potentials to develop a rosin industry which could be treated as a by industry of her developing paper industry.

Chapter One

I N T R O D U C T I O N

1.1 Paper:

Paper is made from cellulose fibres. These fibres are of plant origin. The plant materials are first chemically treated to remove unwanted lignin leaving the plant cells together with the fibres.

The largest source at present is hardwood and softwood of which the pine species (softwood) are on top of the list. Other sources are the bamboos, jute, hemp and sisal hems. Factory wastes like linen and cotton wastes are also used. Low strength papers are made from monocotyledon stalks such as maize, sugar cane and straws from various cereals.

The fibres are suspended in water which is later removed by drainage to give a wet-mat. This mat is weak so it is dried to develop the strength properties of paper. Chemically the fibres consist of cellulose: long chains of D-glucose units, linked together by 1-4 β bonding. The fibres are held together by interlocking in a sieve like manner and also through hydrogen bonding¹.

Initially the bonding is between OH-groups on the cellulose fibres and the water molecules but when water is removed, the much stronger interfibre bonding develops. (Fig.1).

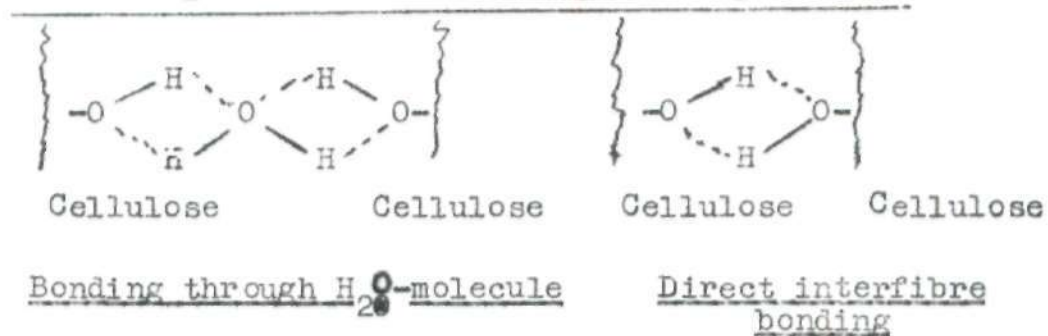


Figure 1

The admissible surface of the cellulose fibres can be increased by fibrillating¹ the fibres in the so called beating¹ process. By this the number of OH-groups available for hydrogen bonding is greatly increased. This increases the strength of the paper and infact the grading of paper into different qualities of different strength properties depends on the extent of fibrillation done on the fibres.

Paper with its interlocking fibre network has pores through it and it is through these pores that aqueous solutions pass during absorption. The cellulose fibres themselves have lumens in them. This means that penetration by water is possible in the plane of the paper and perpendicularly in the paper in the direction of the

inter-fibre pores. The movement of aqueous inks in the plane of the paper surface gives feather-like patterns called 'feathering'¹.

The rapid penetration of water into paper has been explained in many ways. Some believe that because the OH-groups on cellulose possess high affinity¹ for water, they easily form hydrogen bonds with water during the absorption process.

Swanson² studied the factors that affect penetration of liquids into paper. He concluded that the general equation for the penetration of liquids into capillaries and other porous materials holds for penetration into paper sheets also. This equation could be written thus:-

$$\Delta P = \frac{2\sigma \cos\theta}{r} \dots\dots\dots(1)$$

Washburn studied the phenomenon and he gave an equation for the rate of penetration which could be written as below:-

$$\frac{dl}{dt} = \frac{\gamma \sigma \cos\theta}{N \sqrt{4l}} \dots\dots\dots(2)$$

Where in both equations;

ΔP is the difference in pressure across the sheet

σ is the surface tension of the liquid

θ is the contact angle between the paper surface and the liquid-air interphase.

γ is the radius of the capillary

l is the depth of liquid penetration

N is the viscosity of the liquid

$\frac{dl}{dt}$ is the rate of penetration of the liquid

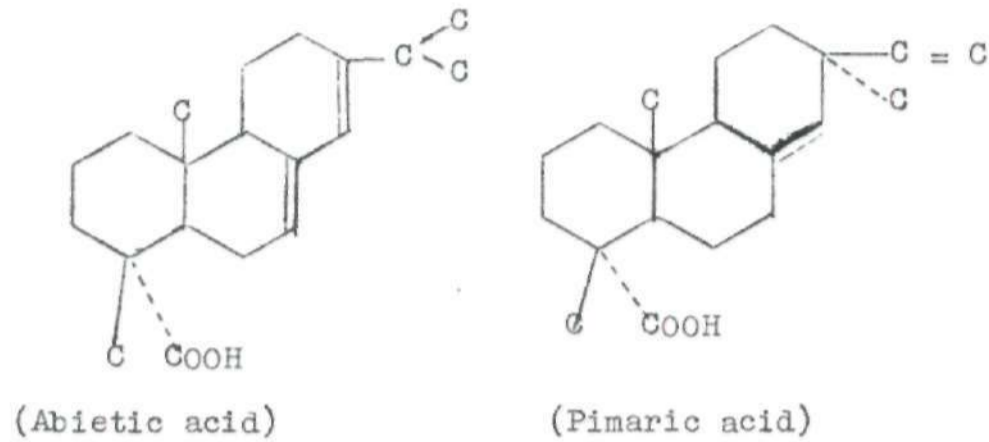
Equation 2 shows that liquids with large contact angles penetrate less. Water and other aqueous solutions possess small contact angles hence rate of penetration is high.

To prevent feathering of inks, on writing papers and disintegration due to loss of strength when ^{water} is absorbed (i.e. in paper bags etc), water absorption must be minimized. One of the ways could be by increasing the contact angles between cellulose and water by treating the cellulose with chemicals that are hydrophobic in nature, e.g. rosin. The process of minimizing water penetration into paper is called sizing².

1.2 Sizing of paper:

This can be done by adding rosin in its salt form into the pulp slurry. The rosin is obtained from the oleoresin of pinus species and consists of about 90% resin acids: isomers of abietic and pimaric acid. (Fig. 2)¹. The remaining 10% is a neutral fraction. Dispersion of the free acids in water is impossible hence acids are saponified¹. The rosin is then said to be cooked. This

This cooked rosin is easily emulsified in water and its dispersion in the pulp slurry is enhanced.



Typical rosin acid structures

Fig. 2

For cooking of rosin, sodium carbonate or caustic soda is used. Usually the practice in the paper factories using this type of process is to add less than the stoichiometric amount of alkali needed for complete saponification. The resulting type of emulsion is claimed to possess better sizing properties than completely neutralized emulsions. The cooking reaction can be represented by:-



This greater sizing ability of this non-neutral emulsion can be attributed to the highly hydrophobic nature

of the free rosin acid molecules present. These form a nucleus on whose surface saponified rosin acids are arranged with their -COO^- groups directed outwards. Since there is repulsion of similar charges from neighbouring similar aggregates of rosin, there is extensive dispersion of rosin particles in the emulsion hence better sizing results are obtained.

To fix the rosin acids onto the cellulose fibres, precipitating agents are needed. These precipitating agents are usually ions of the polyvalent metals. The effectiveness of these ions increases with the valency and the co-ordination number of these metals³. Out of these metals aluminium enjoys a unique position. It is added in the form of alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), a readily available and cheap salt. The aluminium salts are mostly colourless which is important for the making of white paper products (cf. iron gives brown colourations)³.

Studies have shown that optimum sizing is achieved within a limited pH range. Some workers^{4,5,6} have reported that a pH range of 4.0 - 4.5 is optimum for rosin sizing.

It is known also that with an increase in rosin concentrations, there is a corresponding increase in sizing values, however Verhoeff² and his co-workers found that after an addition of 1.0 - 1.5% rosin calculated on dry

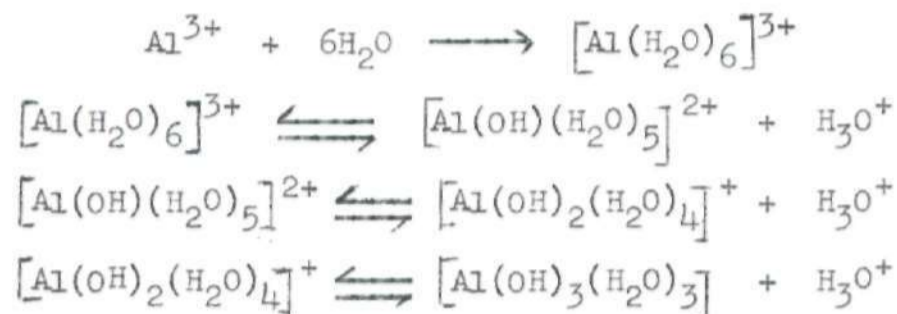
pulp weight, the increase in sizing values obtained per unit weight of rosin is small. The exact amount of rosin at which this saturation phenomenon starts, varies with pulp types and the type of process being used in a paper factory. Obviously this saturation point has to do with the available fibre surface to be covered with rosin molecules.

Strazdins¹ has proposed an electrostatic explanation for the fixation of rosin to the fibres. In his opinion the precipitating agents react with rosin to give a positive charge to the emulgated particles. Next the positively charged particles are attracted by the negative sites on the fibres. If the theory is correct, then an increase in alum addition should cause an increase in sizing values till a saturation point is reached.

1.3 Theories of 'Sizing'¹:

When rosin or alum are added separately to pulp samples, very little or no sizing is achieved, whereas addition of both together to a pulp sample gives a rapid increase in sizing values. The reactions taking place between rosin, alum, and cellulose have been divided into two;

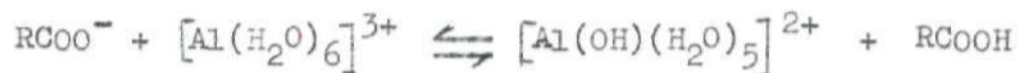
(1) Complexes are first formed between rosin soap and alum. The alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) dissociates into $\text{SO}_4^{=}$ and Al^{3+} ions. It is assumed that the Al^{3+} ions are hydrated and these hydrated ions are hydrolysed to give positively charged complexes as follows:-



This hydrolysis sequence is accompanied by a rapid increase in the acidity of the system. The $\text{SO}_4^{=}$ ions also react with the hydrated Al^{3+} ions as follows:-

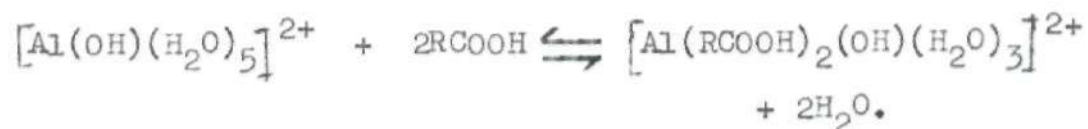


Davison⁷ suggested that rosin in its ionized form (RCOO^-) can also react with the aluminium ion complexes. The aluminium ion hydrates progressively loses its water molecules as was the case with its hydrolysis.



In Taubes¹ opinion a direct attachment of the OH-groups to the aluminium atom reduces the binding effect on the remaining co-ordinated water molecules and so they are rapidly replaced by more rosin molecules to give

di-resinates e.g.



The free rosin acids formed above and the di-resinate molecules are insoluble in water. They flocculate to give sizing precipitate particles. Resinate ions (RCOO^-) attached to the neutral fractions also take down these neutrals with them. Positive charges are imparted to the particles by aluminium complexes aggregating on their surfaces.

(ii) When the size particles have been formed, they are fixed onto the negatively charged fibres. Since these size particles are positively charged, Oswald and Lorenz¹ also assumed that fixation is electrostatic in nature.

This fact has been tested by Strazdins, Mason and Thorde⁶ by observing the movement of particles in rosin/alum emulsions in an electric field. Small fibre debris were found to migrate to the anode in the same type of studies by Strazdins using pulp suspensions.

The $\text{SO}_4^{=}$ competes with resinate ions (RCOO^-) to form complexes with $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$. This competition acts as a moderator for the di-resinate formation. This gives

time for better dispersion of rosin in the system before they are absorbed. This is important in the paper making process where rosin emulsion is added to large chests of pulp. This delay in diresinate formation allows thorough mixing of rosin and pulp before the actual sizing takes place. This avoids local excess of rosin. *on U.*

Precipitation of rosin in acid medium has been observed by Strazding, however the precipitates are negatively charged and cannot be used to size paper effectively. However he observed that when these type of precipitates were used, there was little increment in sizing value and this he attributed to the hydrophobic nature of the rosin acids which enables them to escape from the aqueous medium and adhere onto the cellulose fibres with the aid of Van-der-Waals forces.

If the rosin is to be fixed permanently onto the fibres, forces other than electrostatic attraction and Van-der-Waals' forces must be considered. It has been suggested that the carboxyl groups on the lignin residues and the hydroxyl groups on the cellulose fibres could be used for this purpose. The binding between those groups and the aluminium ions could be co-ordinative in character.

1.4 Scope of present Work:

In the present work it is intended that the retention of rosin and aluminium under various conditions should be studied. The study would be carried out for imported and locally collected rosin samples. It is then hoped that a comparative study of the data would throw some light on the optimum conditions needed for best sizing development. An insight into the mechanism of sizing could also be gained. For the studies the variables were chosen as follows.

pH:

As indicated in the first part, pH plays a great role in sizing of papers and it is a well known fact that sizing values are highest with a certain pH range. It is intended that the work should indicate the area of this sizing pH range by estimating the quantities of rosin and aluminium present on the fibres and in the filtrate got from filtering the pulp slurry as is done on a paper-machine wire. This filtrate is called 'backwater'. The estimation is done at various pH values.

Rosin and alum concentrations:

A variation in the amounts used should affect the sizing values. The pattern of this effect is not well known. Estimation of their quantities in the sheet and

backwater at fixed pH value should show the nature of the relationship that exists between sizing and the above named chemical concentrations. The concentration of one must be fixed while the other is varied during the studies.

1.5 Rosin consumption and production in Nigeria:

Consumption:-

Various industries like the producers of varnish, paint, and furniture polish consume rosin, but so far the largest consumer is the paper industry. In the United States, this industry consumes about 60% of the total rosin produced. The rosin is consumed either in the native form or in forms modified by substituting the hydrogens in the rosin acid rings. These modified rosin products are becoming popular due to their effectiveness per unit weight and their increased solubilities.

Efforts have been made to find other sizing materials to substitute for rosin, but so far none has been able to replace rosin and its derivatives in the whole field of application.

Until now Nigeria imports most of her paper needs. Only 20% is made in the country. The rate of paper consumption goes hand in hand with a country's development. This will account for the rapid growth of Nigeria's paper industry. This growth is indicated by the efforts of

the Federal Military Government to increase the output of the paper industry. Apart from one planned mill for the production of newsprint in which no rosin is used, one other mill using rosin will be started in the current five year development plan (1975-1980) with a capacity of 100 Tons of paper daily.

The existing mill at Jebba produces 14000-15000 tons of paper per year, and assuming a maximum rosin content of about 2%, the rosin consumption at present amounts to 200-300 tons rosin per year in paper making. Allowing another 200 tons of rosin per year for other industries, a total of about 400-500 tons of rosin could be estimated for Nigeria's present annual consumption.

If the expansion programme is carried out, reasoning on the same basis as above leads to a rosin consumption of about 1500 tons/year in Nigeria paper mills only.

Sources of rosin:

Rosin is produced from exudates of pine species. Incidentally, these trees also are sources of long fibre-pulp which is one of the raw materials for paper. Technically the exudates are called oleoresin. Analysis of this oleoresin⁸ from different pine species showed a mean rosin acid content of about 68%, a turpentine content

of about 20% and about 12% water and neutral fractions. The oleoresin composition will differ slightly from that obtained from pines grown in Nigeria due to soil and climatic conditions.

In Nigeria pines do well between latitudes 7° - 10° ⁹, where the difference between wet and dry seasons is less pronounced as it is near the south of the country.

Jackson^{9,10} showed that pines in Nigeria grow best in area where the height above sea level is about 1000 meters with a rainfall not less than 1250mm per year. Heavy rainfalls would compensate for low altitudes.

Growth trials^{10,9} have been carried out in the following areas:-

The Jos plateau
 Kaduna (600 metres with 1300mm rainfall/year)
 Ibadan (210 metres with 1700mm rainfall/year)
 Mambilla plateau (1500 metres with 1700mm rainfall/year)

In all these places the species with best growth rates are the Pinus Oo-carpa Schudle and Pinus Caribaea-var-hondurensis-Barr.

On the same trial sites, Callistris glauca (another conifer type) produces copious exudates of oleoresin with high rosin acid content but its rate of growth is slow. Besides the yield of pulp per ton wood is very low for

this species due to the heavy branching. This suggests that plantations of Callistris glauca could be considered a secondary source of rosin. As rosin industries are by-industries of pulp production, primary sources will be fast growing trees with high pulp yields.

Technical methods for the production of rosin:

Generally three methods are used:

- From standing trees
- Solvent extraction of wood wastes
- Acidification of residual liquors from the pulp mills.

Where standing trees are involved¹¹, wounds are made on the trees and the gum is collected. This is the oleoresin. The syrupy juice is cleaned by filtration and subsequently sprayed in a flask-dry tank, where volatile components like turpentine and water are driven off. The molten rosin falls into a buffer storage tank and is subsequently packed for sale. This method can be used before trees are felled for pulp making.

In the solvent extraction¹¹ wood wastes obtained from pine Stumps uprooted from pine plantations are chipped to convenient sizes. They are then extracted with naphtha or petroleum of 200^o-240^oF boiling range. Subsequently the solvents are removed in evaporators. A suitable source

of these solvents is the Nigerian petroleum industry.

The last method is only applicable where pulp is made from pine wood exclusively. The residual liquor¹¹ filtered off contains rosin soap. Acidification of this liquor liberates the free rosin acids. These are skimmed from the surface of the liquors.

Production of rosin in Nigeria:

The first two methods of production are suitable for Nigeria. Infact these two methods could be integrated by feeding the pre-heated oleoresin of the first method into an intermediate evaporator together with the oncoming wood extracts from the second method.

The last method of rosin production will not be useful in Nigeria since it is planned that a mixed cook of pines and hardwoods would be used to make pulp. This means that purification of the rosin soaps will be expensive.

From this brief study, one can conclude that Nigeria has the potentials to produce her own rosin. Also there is an expanding market for rosin in Nigeria. This market could possibly be extended to the neighbouring countries. Lastly the petroleum industry will provide a cheap readily available source of solvents for the rosin production.

Chapter Two

RAW MATERIALS AND EXPERIMENTAL METHODS

This chapter will deal with raw materials used and the selection of laboratory methods that would be used in the work.

2.1 Raw Materials:

Imported rosin (This is gum rosin made in Portugal). This was supplied by the Paper Mill at Jebba. The lumps of rosin with a brown crystalline appearance were kept in sealed cellophane bags to exclude air and moisture. Generally commercial rosin is graded¹² on basis of colour represented by letters X, WW, N, M, K, I, H, G, F, E and B in order of increasing darkness and decreasing quality.

Analysis of different grades showed that they possess acid numbers¹² ranging from 120 to about 160. Here acid number is used to characterize rosin. It is the number of milligrams of potassium hydroxide required to neutralized one gram of rosin. The best qualities have the higher acid numbers. Rosin samples contain the rosin acid fraction (abietic and primaric acids and their isomers), fatty acids, and neutral fractions in various proportions but rosin acid content varies from 60-90%. The quality of rosin increases with content of rosin acids.

Our analysis of the imported rosin given gave a rosin acid content of about 60%. Analysis was done by precipitating the acids with cyclohexylamine. Comparison with a rosin colour chart showed it to be of grade WW.

60 The acid number and moisture contents were about 170 and 0.5% respectively.

W Nigeria (local) rosin - This was produced by wounding pines at Afaka plantation in Kaduna. The species used were the Pinus-Oo-Carpa and Pinus Caribaea-var-hondurensis -Barr⁹. The exudates also called oleoresin were collected in little containers made of aluminium foil. Exudates production in a particular wound could last for about 3-5 days. Rosin acids dissolve in organic solvents like ether, chloroform and acetone. This property was used in isolating the rosin acids from the oleoresin samples collected. In our case, the oleoresin was treated with ether and the solution filtered under suction. The ether extract was evaporated to dryness in a beaker on a steam bath. The residue was very sticky and on standing overnight in a desiccator, it gave a mass of pale brown crystals. This product is our local rosin.

Analysis of the local rosin made showed a moisture content of about 6.3% with an acid number of about 150.

The rosin acid content was determined by precipitating the acids as cyclohexylamine¹³ salts. This gave a value of about 55%, but calculations using observed acid number gave about 68%. This difference between the two methods was due to incomplete precipitation of the cyclohexylamine salts. It was observed that filtrates obtained after filtering off the salts went turbid on standing due to further salt precipitation. This indicated that this method is good only for qualitative work.

Comparing the local rosin colour with a rosin colour chart showed it to be between N and M grades.

Since rosin is insoluble in water, effective distribution in paper-making systems is obtained by making emulsions of rosin soaps. Soaps are made by a saponification process¹⁴ as follows:-

Rosin (5.0gms; 3.3m moles) was treated with a slight excess of sodium carbonate analytical grade of 99.9% purity (1.0gm; 8.93m mles) in distilled water (70 mls). The resulting mixture was transferred into a round bottom flask (250 mls) and diluted with water (100 mls). It was then boiled under reflux for two hours. During this process the rosin gradually dissolved to give a brownish liquid which was transferred into a two litre flask and

made up to two litres mark with warm distilled water at 60°C. This converted the reaction mixture into a white emulsion which was used as the rosin stock emulsion with a concentration of 0.25%.

Alum Sample - (Brand - Boliden Aluminium sulphate)
 (Supplier - Boliden Aktiebolag of Sweden)
 (Al₂O₃ content is about 17-18% and is
 iron free).

Commercial alum crystals given by Jebba Mills were also used for the studies. A 0.2% stock solution of the alum was prepared in distilled water. The hydrated form of the crystals contained various amounts of water molecules which could be represented as Al₂(SO₄)₃ · XH₂O where X is claimed to be about eighteen in paper maker's alum¹.

Pulp sample - (Billerud unbleached Kraft Pulp)
 (Supplied by Billerud of Sweden).

The pulp samples used were wet unbleached kraft pulp given by the mill at Jebba. The pulps were semi-refined to a freeness¹⁴ of about 25-30°SR where °SR is the degrees Schopper Riegler. Freeness is the ability of a given pulp to retain its water contents and it is measured by the rate of drainage on standard sieves. Freeness is measured by reading the volume of water that drains into a cylinder graduated into 100 parts with markings starting

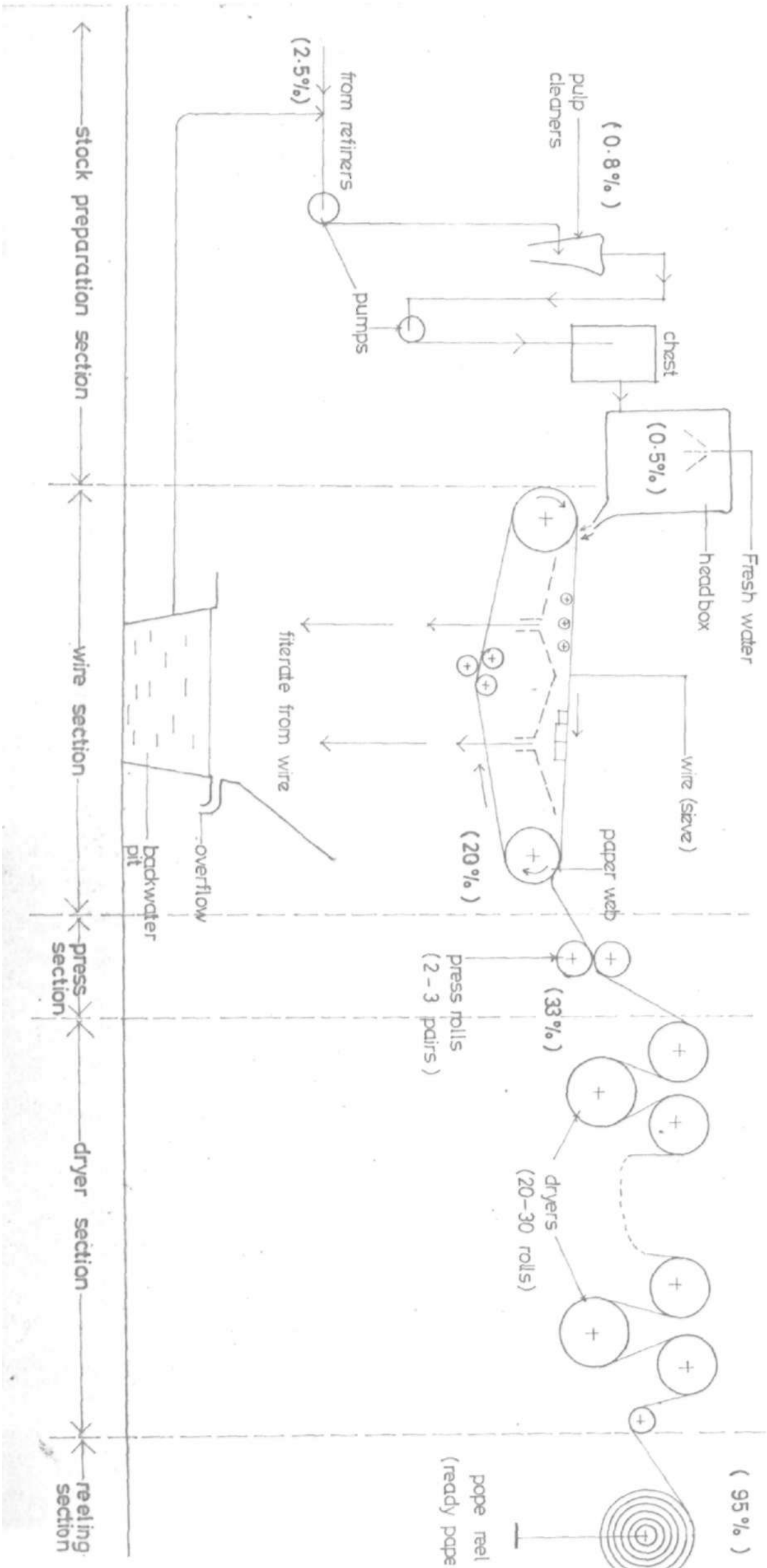
from top to bottom. The procedure and conditions are contained in the standard methods of the Technical Association of Pulp and Paper Industries (Tappis). The higher the $^{\circ}\text{SR}$ value, the slower the rate of drainage of water from the pulp. The rate of drainage depends on the number of cellulose hydroxylic groups that are available for making weak bondings with water molecules. This number is directly proportional to the surface area of the pulp fibres exposed during refining. The wet samples were stored in a fridge to prevent biological decomposition.

2.2 Preparation of hand Sheets:

The effectiveness of a given rosin sample is best evaluated by making paper, sized with the rosin sample on a paper-machine.

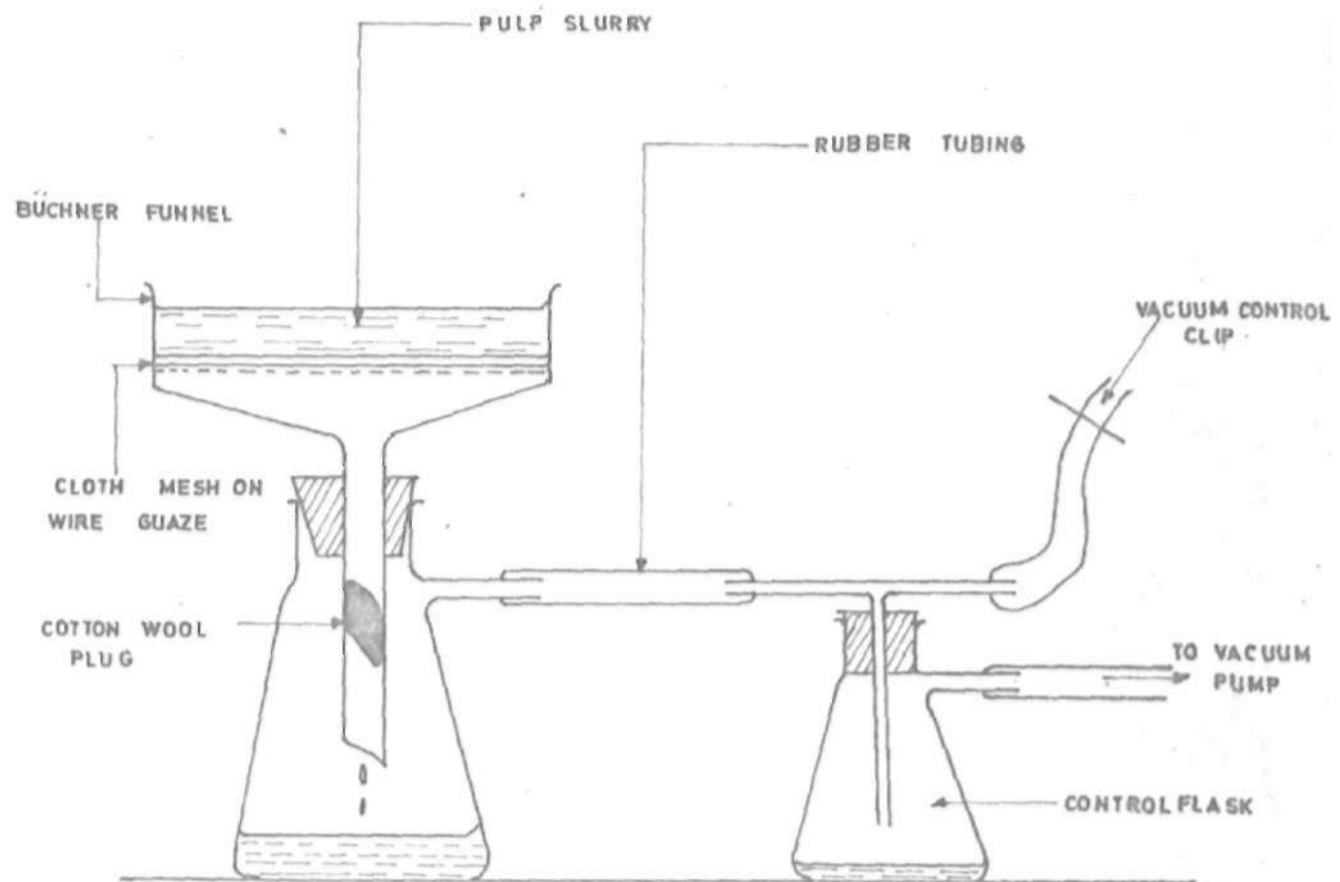
This approach is not feasible for a systematic evaluation of a large number of samples within a reasonable time since equilibria in paper-making systems are not quickly established. The size of a paper production unit and the partial circulation of the enormous quantity of water used in the paper making are causes of the long delay before a state of equilibrium is re-established after a change in the addition of any of the paper making

THE PAPER MACHINE SYSTEM FIGURE 3



ARRANGEMENT FOR PREPARING HAND SHEETS

Fig 5



(iii) processing of the wet paper mat between press rolls to smoothen the paper and to remove part of the water.

(iv) Drying of the paper on drying cylinders.

The paper making process is imitated on a laboratory sheet former by draining a pulp slurry with a solid content of about 0.4-0.5% on a wire gauze (See figure 4). Subsequently the gauze with the sheet is removed from the apparatus. The sheet is taken off the gauze, pressed with a hand roll and dried between blotting paper, and dried on laboratory drying cylinders. The resulting sheet is called a hand sheet.

The essential difference between paper making on a sheet former and on a paper machine is that on the latter the fibres are orientated during drainage of the pulp in the direction of the speed of the wire (machine direction). Paper thus produced will show different characteristics in the machine direction and in the cross direction. These differences are most pronounced in the strength properties. Properties like water absorption are influenced by the direction of measurement to a much lower extent. As a consequence the laboratory sheet former on which the fibre orientation is at random in the horizontal plane gives more reliable results for water absorption properties

than for strength measurements of hand sheets in relation to the results obtained in the practice of paper making.

The experimental work for the underlying investigation could not wait for the arrival of a laboratory sheet-former in the department so we made our own arrangements as sketched in fig.5.

h In the arrangement a Büchner filter funnel represented the cylinder in the sheet former. Similarly the wire gauze was replaced by a fine mackintosh cloth mesh supported on a coarse wire gauze.

d: To retain the pulp slurry on the wire gauze before drainage starts, a cotton wood plug which had been soaked in water for one day was inserted as shown in figure 5. This represented the valve shown for the sheet former in figure 4. In the sheet former the drainage is carried out by opening the valve and also that of the sump so that water flowed out so draining the pulp. In our case we used a vacuum pump to drain the pulp.

According to the practice of paper making the weight¹⁵ of sheets (or paper samples) is expressed in gram per square meter (GMS). The water drained in the three methods of making paper is called backwater or white water. This water contain residual materials not adsorbed by the

fibres in the sheet. Also in the three procedures mentioned the pulp slurry drained on the wires had a consistency of about 0.4% where consistency is the percentage by weight of bone-dry pulp in a given pulp slurry .

The funnel used had a radius of 10.6 cms hence an area of 353 sq. cm. This meant that a paper sheet of 60 grams. per square metre (60 GMS) should weigh about 2.12 gms when prepared with the funnel. Throughout this investigation sheets of 60 GMS were prepared and tested.

Pulp samples were disintegrated in a plastic bucket using an electric stirrer. This operation took about 1-2 hours depending upon the dryness of the pulp used. Distilled water was added and sheets were prepared using a fixed volume of the pulp slurry. These sheets are used to determine the concentration as percentage of bone dry pulp in a fixed quantity of pulp slurry. The consistency of the stock pulp slurry was found to be about 0.5-0.8%.

Quantities of this slurry that would give 2.12 gms sheet in the Buchner funnel were taken into a two litre plastic jug and treated with rosin needed, then stirred for one to two minutes with a glass rod. Alum needed was added and the sample was stirred again. The pH of the sample with these additives was about 5.5-6.0. The pH at

which sheets would be made was fixed as described in section 2.3. The slurry was then made to one litre with distilled water to give a final consistency of about 0.35 to 0.50%.

This was quickly but gently poured into the funnel which had been stoppered with the cotton wool plug. The water was removed by suctioning using a vacuum pump. By controlling the rate of suction with the air inlet shown in figure 5 a uniform spreading of the slurry on the wire was achieved. This is called formation of the sheet by paper-makers.

The sheets formed were blotted between filter papers. A smoothing effect produced by the process on the paper machine could be imitated by rolling a piece of iron pipe under light pressure on the upper filter paper layer. The sheets were dried on a photodryer. Since the sheets were more dried than the paper made on a paper machine, they were kept for one day at room conditions. This was done because the initial water contents¹⁵ of the sheets affect their water absorbing properties.

2.3 Variation of pH, Rosin and Alum Concentration:

To study the effect of the variation of pH on sizing 10 mls rosin (25mg) and 10 mls (1.62mg Al³⁺) alum were

added to pulp slurry which gave 60 GSM sheets as above. The pH of the slurry was adjusted to the desired level using a pH meter. Adjustments were made with sulphuric acid (2N; 2-6 drops) or sodium hydroxide (2N; 2-6 drops). The range chosen was from pH 2-6.5. Below pH = 2, the sheets were charred on drying due to high acidity. Even when dried at room temperature they later crumbled to pieces. The upper limit was chosen at 6.5 since above this value this sizing process with rosin is not possible.

For investigating the effect of variation of rosin concentration, the pulp slurry was treated with 10 mls (1.62mg Al^{3+}) alum and various quantities of rosin were used to make sheets at the optimum pH found from the effect of pH variation.

Similar experiments were carried out to investigate the effect of varying the alum concentrations. Here sheets were made with 10 mls rosin (25mg) at the optimum pH. These experiments were performed using both imported and local rosin.

2.4 Determination of Rosin:

Three methods were tried. The last one was found to be useful and adopted as the standard in the work.

Gravimetric method - This method was proposed as a standard method by the Technical Association of the Pulp and Paper Industry (Tappi)¹⁴. Here backwater samples or acidified ethanolic extracts of paper samples were evaporated to dryness and the residues were dissolved in ether. The ether solutions were filtered and the filtrate evaporated to dryness till a constant weight was achieved. The ether residues were assumed to be the rosin present in the backwater or in the sheets. From these, total rosin in 2.12gms of sheet and all backwater collected were estimated respectively.

The results of rosin extracted from the sheets at various alum concentrations and at optimum pH is show on page 32.(Table.1). About 25mg of rosin was added to each pulp sample and corrections were made for the moisture contents of sheets. (Moisture contents of the sheets was about 3.45%).

These results showed that values of rosin quantities determined in the sheet fluctuated strongly and were higher than the amount originally added to the pulp. This error could be as high as 50-60% of rosin added. On this basis the Tappi gravimetric method was discarded. These high values would be due to other materials extracted with rosin.

Table 1: Rosin extracted from sheets

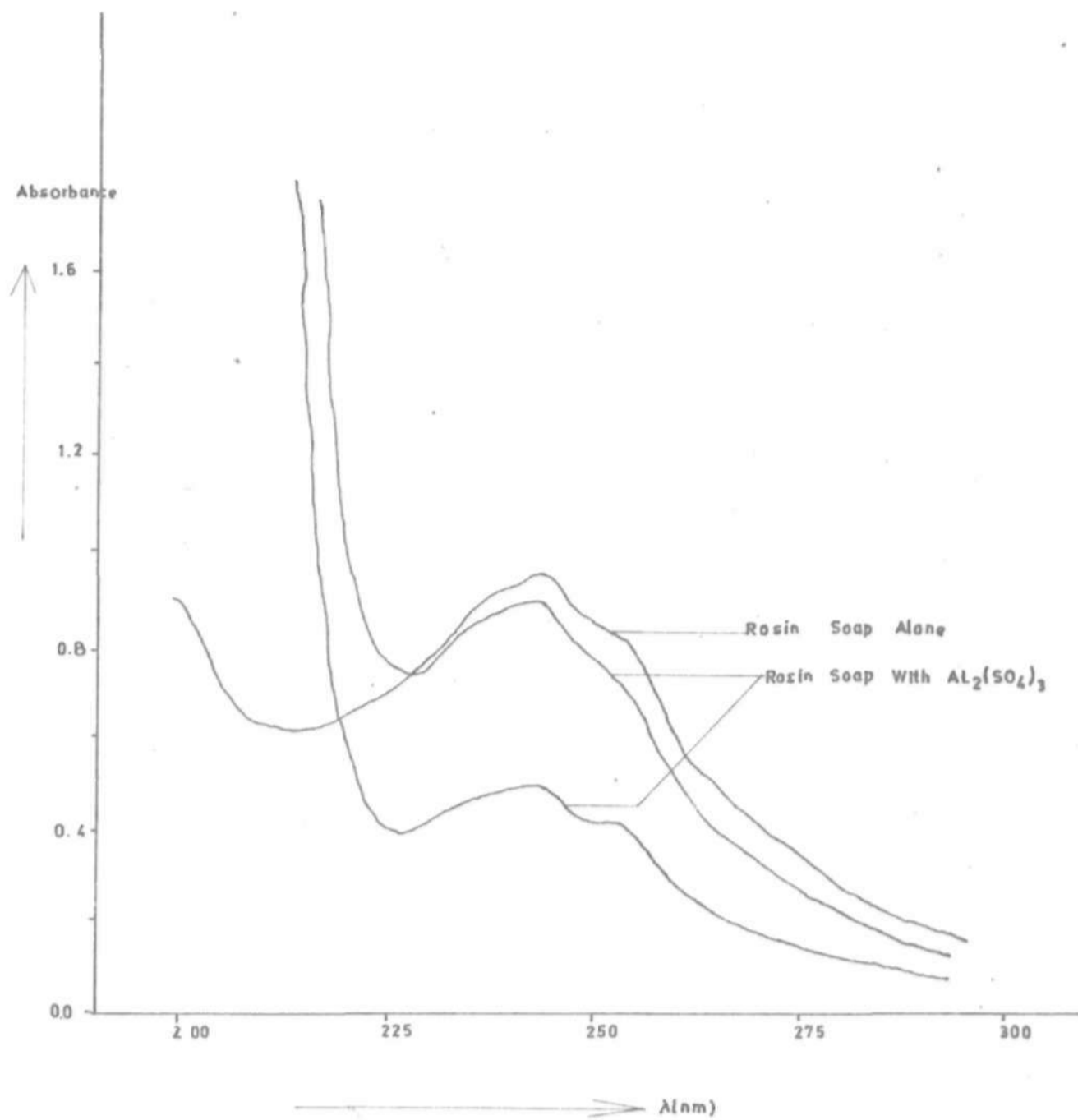
Aluminium added	Weight of residue from 0.5gm sheet (mg)	Total rosin in 2.12gms sheet (mg)
0.0	8.9	39.1
0.33	17.7	77.6
0.49	8.9	39.1
0.65	5.9	26.1
0.97	4.8	21.1
1.30	8.6	37.7
1.62	9.3	40.8

Colorimetric method:

Verhoeff, Hart and Gallay² used dyes that react with rosin. The dyes and the rosin were first mixed to allow them to react. This dye/rosin mixture was added to the pulp slurry. The amount of dye left in the sheets and backwater were matched against standards.

This method was also not satisfactory since one was not sure whether it was the dye/rosin complex or rosin/aluminium complex that was retained. Such a dye/rosin complex could possibly interfere with the rosin/ Al^{3+} complex formation. It was possible that some of the dye did not form rosin/dye complex and were just washed into the backwater and some sticking unto the fibres. All these fact would affect our results.

UV ABSORPTION OF ROSIN SOAP ; Fig. 6
(AQUEOUS SOLUTIONS WITHOUT PULP)



Spectrophotometric method:

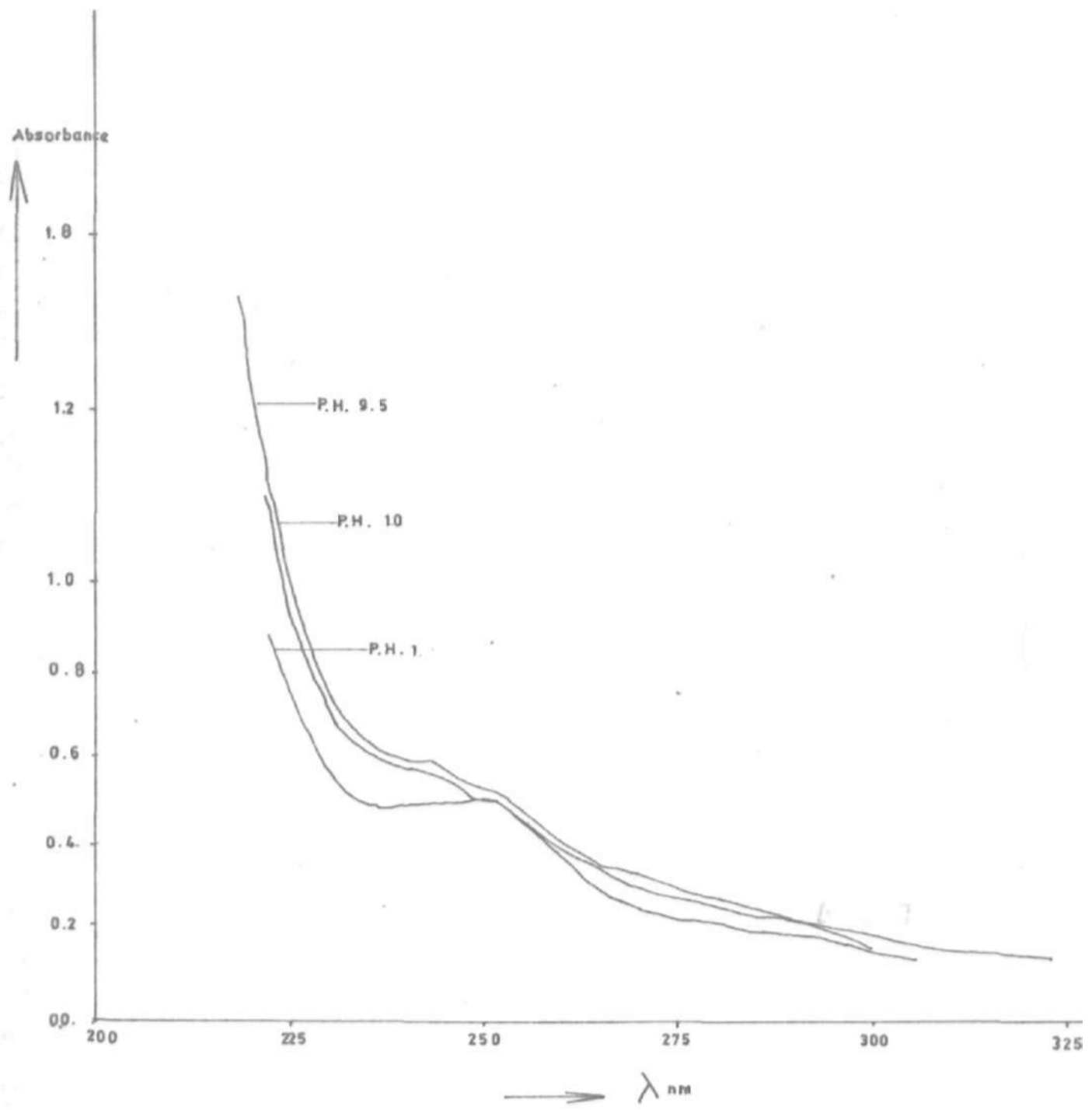
Kami-Pa-Gikyoshi¹⁶ showed that it was possible to determine rosin in the backwater spectrophotometrically. This was possible because rosin absorbs UV-light in the range of 200-300nm^{17,18,13} with different isomers having different absorption peaks.

We tried this method. The spectra obtained for thoroughly defibred backwater samples did not show distinct absorption peaks (See Figs. 6 and 7). This was due to the presence of other wood components dissolved in backwater during sheet making especially at very acidic and alkaline pH values. The compounds seemed to absorb UV light in the same wavelength region as the rosin acids. Some of these compounds¹⁹ were lignin, tannins and protolignins.

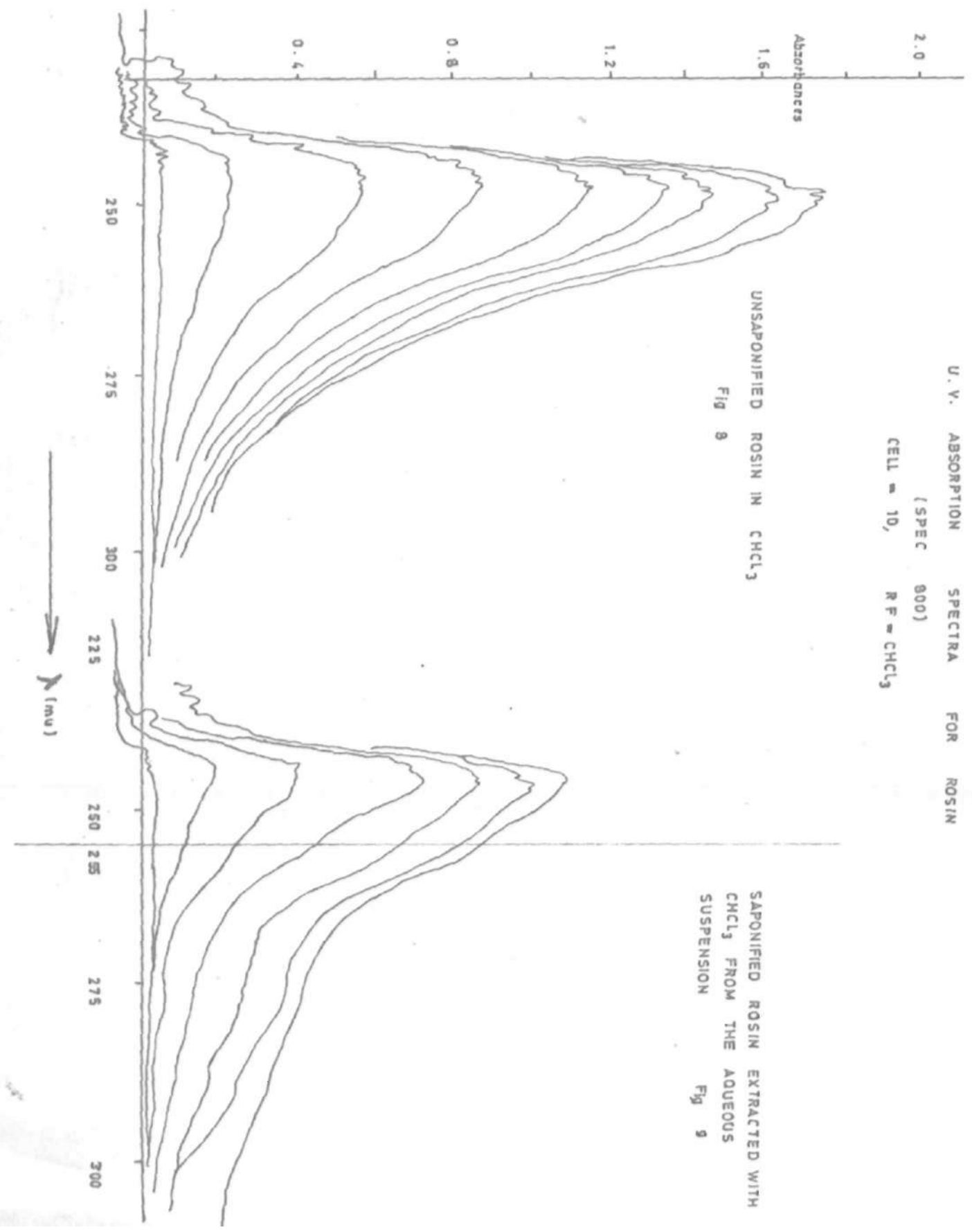
Trials carried out on paper extracts also proved to be unsatisfactory. In the extraction, the acidified ethanol used reacted with lignin to give an alcohol-lignin complex with alkoxyl-groups¹⁹. These complexes were split by the acid to give simpler compounds. These products interfere with the rosin absorption (See Fig. 6 and 7).

In view of the foregoing facts, attempts were made to extract the rosin acids from the aqueous media using organic solvents before the spectrophotometric determination.

U V ABSORPTION OF ROSIN SOAP IN BACKWATER ; Fig 7



U. V. ABSORPTION SPECTRA FOR ROSIN
(SPEC 800)
CELL = 10, R F = CHCL₃



Liquid/liquid extractions (extraction of backwater or paper extracts) were carried out using various solvents such as ether, acetone, chloroform and mixtures of these solvents. Of all extractions tried, the aqueous liquid/chloroform extraction proved to be the most successful. However, the absorption peaks were cut off around 240-245nm due to the strong absorption of chloroform at this wavelength range. This separation was successfully carried out for backwater samples with little interference from other wood extractives. However the extraction with chloroform of ethanolic paper extracts was unsuccessful. The chloroform extracts were brown and did not show proper absorption peaks in the UV-spectrophotometer.

To prove that it was the rosin giving the absorption spectra obtained, pure samples of unsaponified and saponified rosin were dispersed in water and the emulsions were extracted with chloroform (analar grade). Similar spectra were obtained (See Figs. 8 and 9).

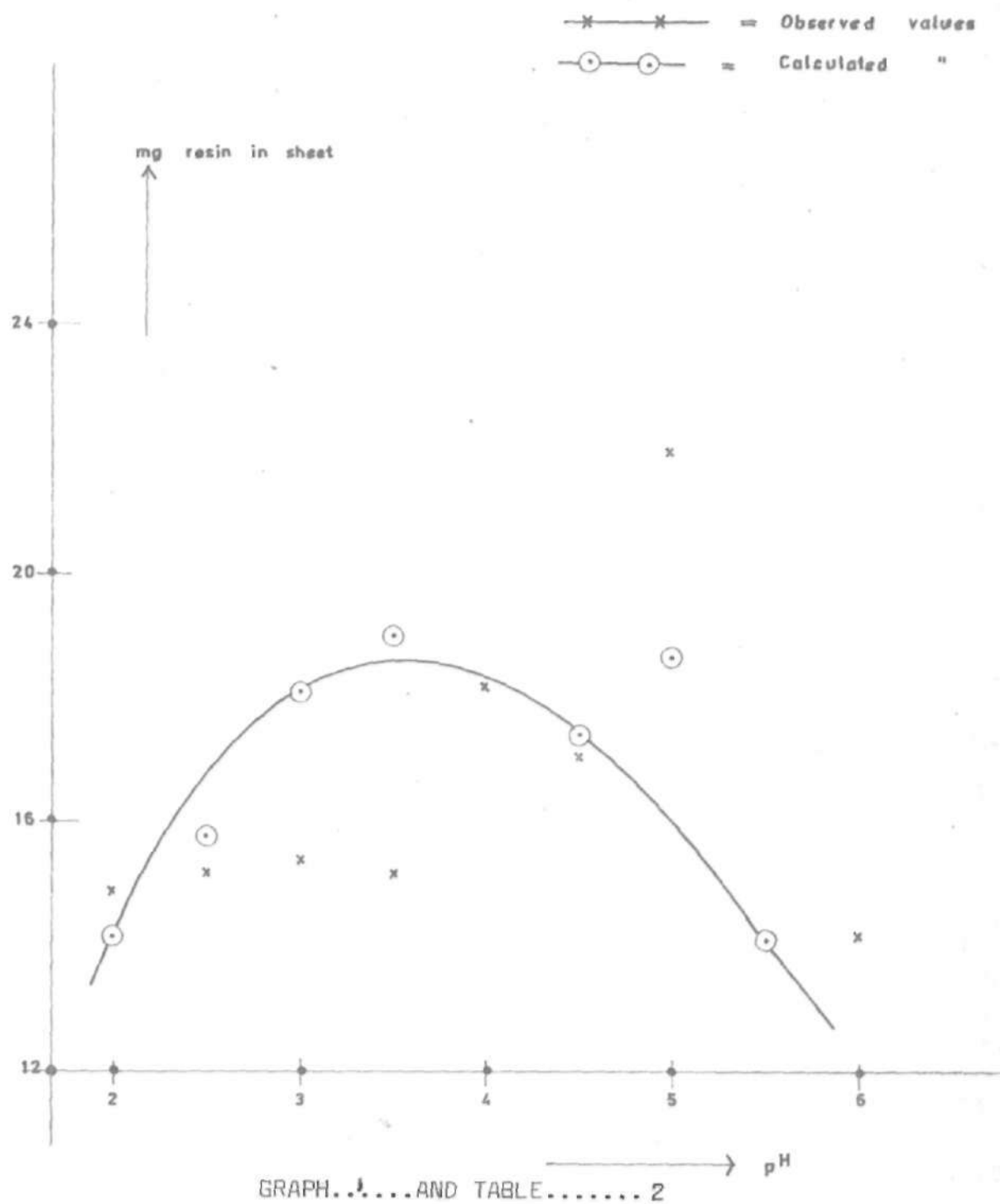
On this basis we decided that a spectrophotometric determination of rosin in backwater after extraction with chloroform would be possible. The preparation of a calibration curve for that determination will be the subject of the next section.

It has been shown in page 37 that the determination of rosin in sheets cannot be done in a similar way. We tried another method by passing the brown chloroform extracts through a column of activated alumina and eluting it with chloroform. The brown colorations were removed, but some rosin was lost as can be seen in Table 2 and Fig.10. The spectrophotometric values were compared with calculated values for rosin in the sheet got by subtracting the rosin in backwater from the amount added to the pulp initially. The measured values were found to be usually low and highly inconsistent.

Table 2: Observed and Calculated rosin in sheet

pH	Absorbance	Rosin observed (mg)	Rosin calculated (mg)
2.0	0.55	14.9	14.1
2.5	0.56	15.2	15.7
3.0	0.57	15.4	18.1
3.5	0.56	15.2	19.0
4.0	0.68	18.2	13.4
4.5	0.64	17.1	17.4
5.0	0.82	22.1	18.7
5.5	-	-	14.1
6.0	0.53	14.20	11.1
6.5	0.79	-	4.9

OBSERVED AND CALCULATED RESIN IN SHEET ; Fig 10...
 AT VARIOUS pH VALUES



It may be concluded that the spectrophotometric determination of rosin in sheets after separation over activated alumina was not satisfactory either. Instead of a determination of the quantity of rosin in sheets we will use a determination of the rate of water penetration in the sheet (3.10).

2.5 Calibration curve for the Spectrophotometric Determination of Rosin:

Portions of stock emulsion of imported rosin (0.25%) were taken and made up to 100 mls with distilled water. Subsequently the pH of the diluted sample was adjusted to about 10-11 with sodium hydroxide (2N). The diluted sample was transferred to a 250 ml separating funnel and 25 ml of analar chloroform was added. The funnel was shaken for a few minutes. After that the chloroform layer was drawn into standard 50 mls flasks. Another 20 mls of the CHCl_3 was used to extract the aqueous layer for the second time. The two extracts were combined and made up to 50 mls. Absorption spectra were recorded with the Unicam spectrophotometer 800 using 10mm silica cells.

At a wavelength of about 255nm all isomers of rosin showed absorption, but different peaks were cut off however due to the strong CHCl_3 absorption in the range of 235-245nm.

In aqueous systems absorption of rosin acids has a maximum at about 241nm. This shifts to about 250nm in chloroform²⁰. We choose 255nm, near to the expected absorption maximum but not hindered too much by the chloroform absorption. The results of the calibration are in Table 3 and Fig.11. A similar calibration curve was prepared for local rosin also.

Table 3: Rosin Calibration curve at 255nm.

Volume of stock extracted	Concentration (mg/lit.)	Absorbances
0.0 mls	0.0	0.00
0.1	5.0	0.10
0.3	15.0	0.25
0.5	25.0	0.44
0.8	40.0	0.66
1.0	50.0	0.81
1.1	55.0	0.88

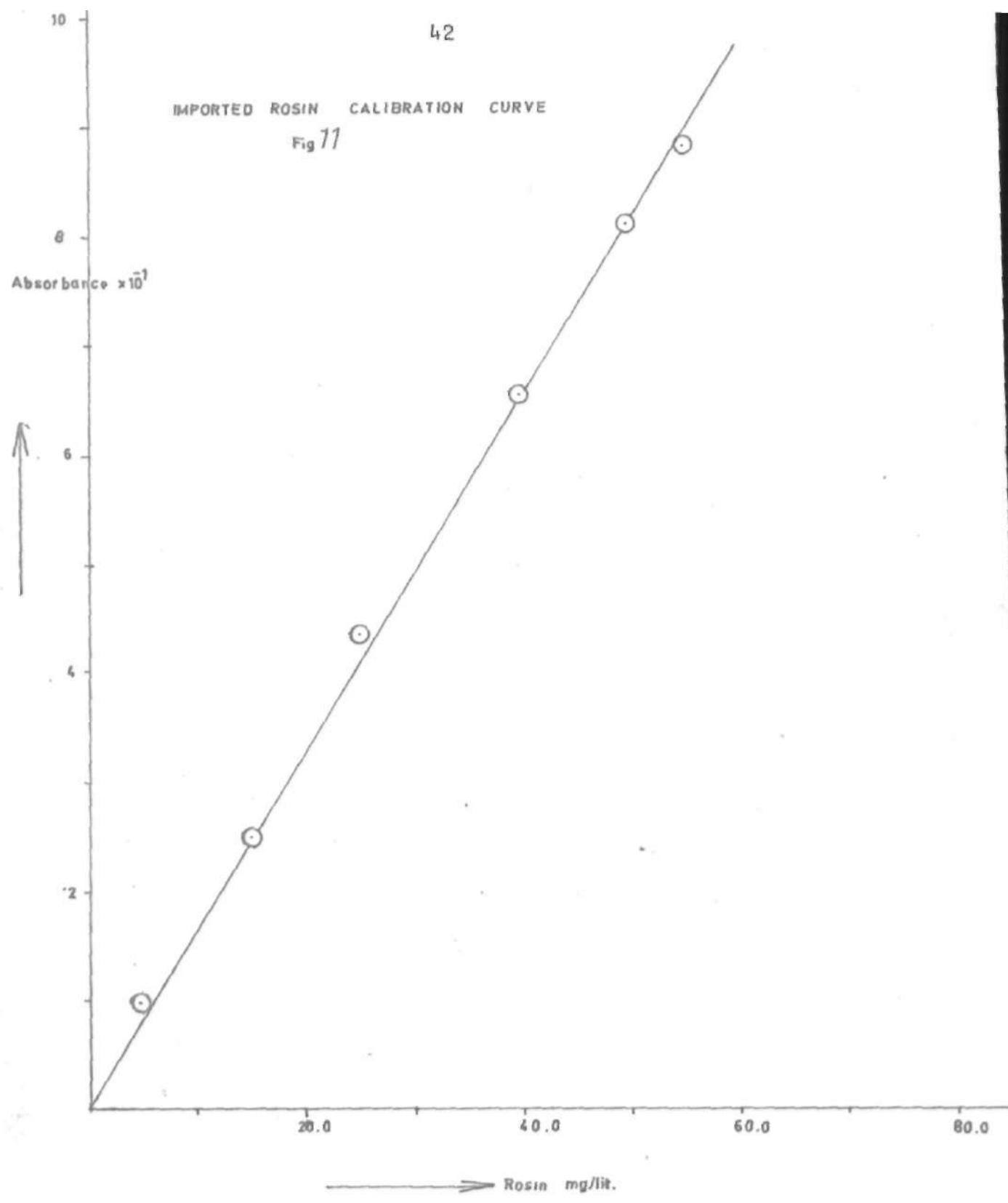
The calibrations for imported and local rosins are shown in Fig.11 and Fig.12 respectively.

2.6 Determination of rosin in Backwater:

Backwater samples were defibred by filtering on cheese cloth under suction. Rosin extraction was carried out as in the previous paragraph for 50 mls of each sample. The rosin concentration were read from the

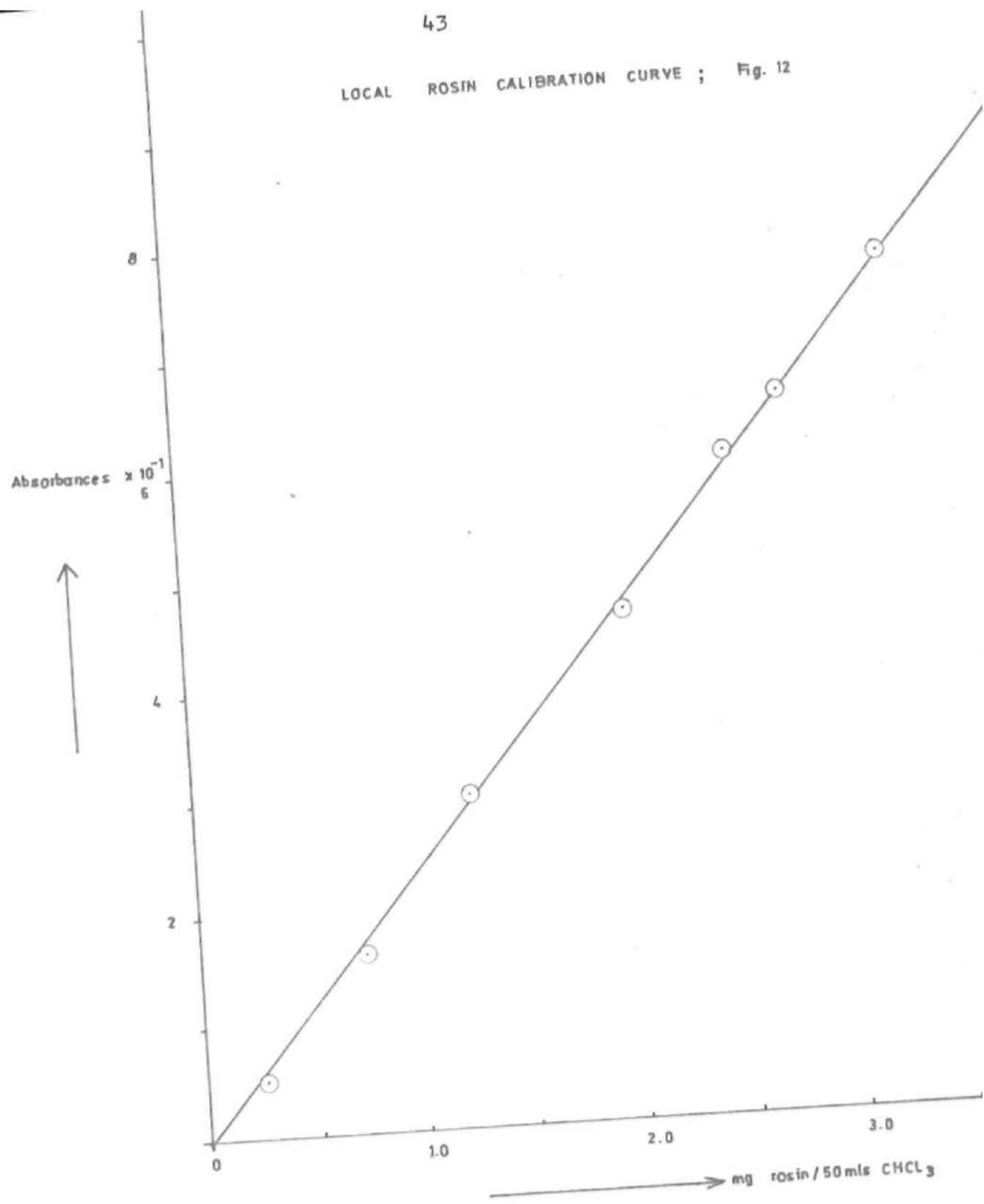
IMPORTED ROSIN CALIBRATION CURVE

Fig 11



GRAPH 2.....IMPORTED ROSIN CALIBRATION CURVE.....TABLE 3

LOCAL ROSIN CALIBRATION CURVE ; Fig. 12



GRAPH 3 LOCAL ROSIN CALIBRATION CURVE TABLE ---)

calibration curve. Separations should be done carefully since little debris of fibres collect at the interphase of chloroform and water. They may interfere with the rosin absorption in the spectrophotometer.

2.7 Determination of aluminium ions:

In general, there are various methods for the determination of aluminium ions including gravimetric²¹, colorimetric²¹ and co-precipitating²¹ methods. Our experience with these results are summarized below.

Gravimetric methods:

Here the aluminium ions were determined as alumina (Al_2O_3). The alumina was obtained by igniting the aluminium hydroxide precipitated under alkaline conditions. We tried this method but did not get reproducible^{21,22} results. Other workers reported the same experience.

The total precipitation of aluminium hydroxide occurs at pH 6.5-7.5. In this narrow range indicators gave no reliable result since end-point colour changes were often difficult to observe. We used a pH-meter. However too high results were obtained (but reproducible). The amount of water of crystallization in ignited alumina is usually a matter of uncertainty as shown by Blum²³. After all the small amount of precipitate in our work caused a comparatively low accuracy of the weighings.

Co-precipitation method:

Here precipitating agents are used to precipitate aluminium ion complexes. The precipitates are weighed and from their molecular formulae the aluminium ion contents could be determined. The common precipitating agents are 8-hydroxyquinoline and solochrome-cyanine-R. We tried these two but the results were not reproducible.

Spectrophotometric method:

Coloured aluminium complexes are used to determine the concentration of aluminium ions by means of a Bausch and Lomb spectronic 20 spectrophotometer. Our trial was based on the method proposed by K. E. Burke²⁴ in 1966. The results we obtained were reproducible and considering the foregoing observations we decided to determine the aluminium contents of our samples in this way.

2.8 Calibration curve for spectrophotometric determination of aluminium ions:

Reagents - About 0.10 gms aluminium wire of analytical reagent grade (99.9%) was treated with concentrated HCl (3 mls) and concentrated HNO₃ (3 mls) respectively. The resulting reaction mixture was heated until a homogeneous solution was obtained. This was diluted to 2 litres with distilled water.

A buffer solution of pH 9.0 was prepared by dissolving 207 gms ammonium chloride in 266 mls concentrated analar ammonia solution, in a 2 litre flask and made up to the mark with distilled water.

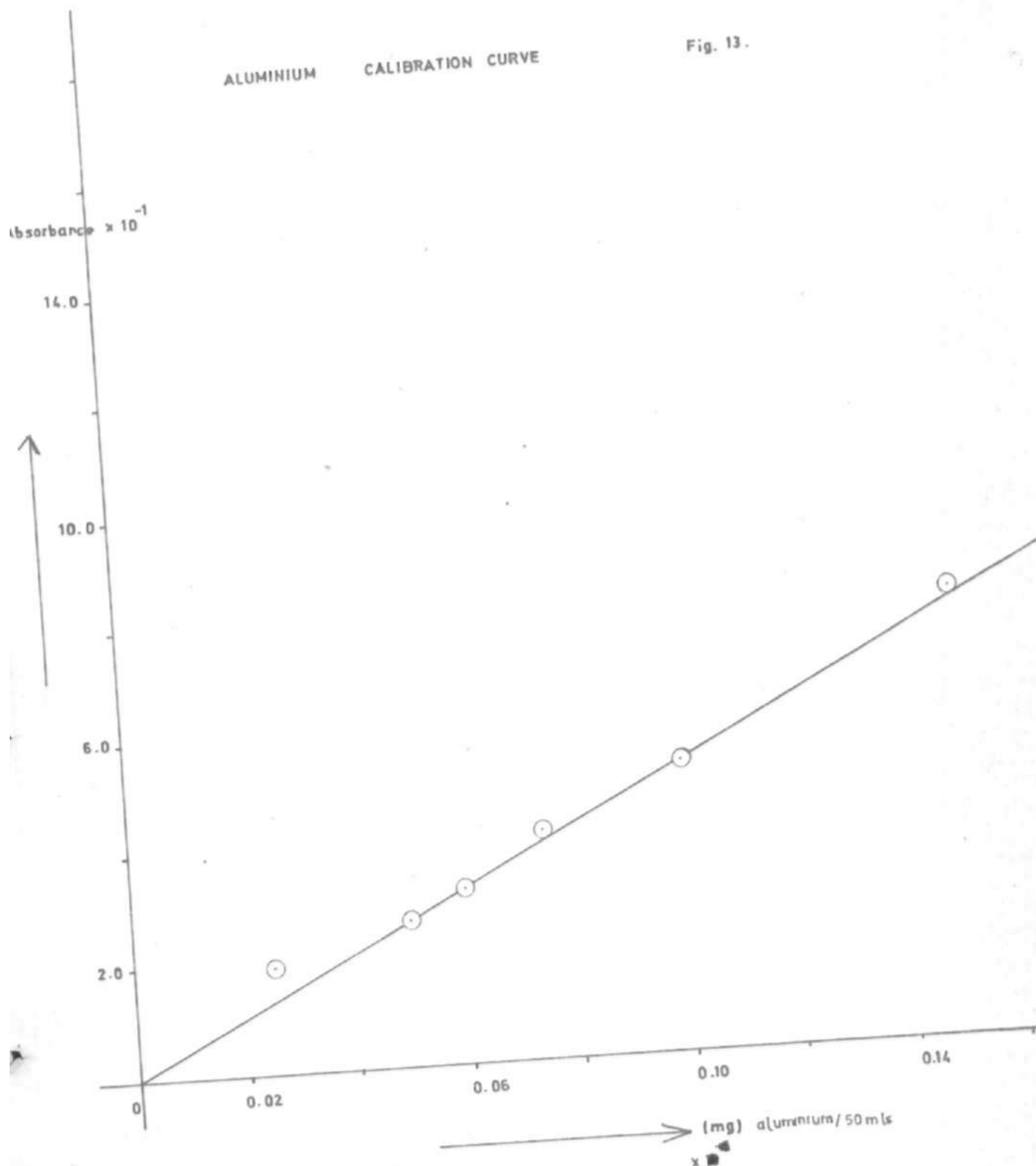
The 8-hydroxyquinoline reagent (1%) was prepared by dissolving 1.0gm of the solid reagent in 100 mls of chloroform. The reagent was stored in a dark bottle.

Procedure of aluminium ion determination:

Portions of the aluminium solution were taken into a 250 mls beaker and 50 mls of distilled water was added. The pH was adjusted with drops of analar ammonia solution or HCl (2N) to give a value of 9.5 on a pH-meter. Then 10 mls of the buffer solution was added and the whole was made up to 150 mls with distilled water. This was transferred into a 250 mls separating funnel and 10 ± 1 mls of the 8-hydroxyquinoline reagent in chloroform was added. The funnel was shaken for about 2-3 minutes. The system reached equilibrium after about two minutes. The CHCl_3 layer was run into a 50 mls standard flask. The aqueous layer was again extracted with another 10 mls of chloroform. The chloroform extracts were combined in a 50 mls volumetric flask and made up to the mark with acetone (analar).

ALUMINIUM CALIBRATION CURVE

Fig. 13.



GRAPH 4 ALUMINIUM CALIBRATION CURVE TABLE 4

An intense yellow solution was obtained. Using acetone as a reference, absorbances were read at 390nm with Baus'ch and Lomb spectronic 20. A blank extraction with distilled water was done and its absorbance value subtracted from the aluminium determinations. A graph of absorbance values against concentrations was prepared. (Table 4 and Fig. 13).

Table 4: Aluminium calibration curve at 390m μ

Stock Solution extracted	Absorbance	Corrected Absorbances	Concentration mg/50 mls
0.0 mls	0.04	0	0.0
0.5	0.23	0.19	0.025
0.8	0.25	0.21	0.040
1.0	0.30	0.26	0.050
1.2	0.35	0.31	0.060
1.5	0.45	0.41	0.075
2.0	0.57	0.52	0.100
3.0	0.84	0.80	0.150
4.0	1.09	1.05	0.200

2.9 Determination of aluminium ions in backwater and in Sheet:

Backwater samples (30-50 mls) were taken and HNO₃ (2N) (3 mls) and HCl (2N; 3 mls) were added respectively. The mixture was made up to 100 mls with distilled water and then boiled for about three minutes until all the fumes

of the acids were discharged.

The solution was then cooled in an ice water bath and the pH was adjusted as in the procedure for the calibration curve. Subsequently the aluminium ion concentrations were determined with the Baus'ch and Lomb Spectronic 20 and the calibration graph, following the procedure of the previous paragraph.

To determine the aluminium ion content in the sheets, weighed samples corrected for moisture content (about 0.5gms) were ashed in silica crucibles in a muffled furnace at about 1000°C. The ashes were dissolved in HNO₃ and HCl and the aluminium ions content determined as above.

2.10 Rate of water penetration in Handsheets:

Since 'Sizing' is done to minimize the rate of penetration of aqueous liquids into paper, the most direct way to evaluate sizing is that based on rates of penetration of these liquids.

In this work paper samples were floated on a 1% solution of ferric chloride. A drop of potassium ferrocyanide (1%) was placed on the sheets. When the two solutions made contact, the blue colour of the Ferriferrocyanide complex developed immediately.

The paper sample was put on the FeCl_3 solution and the drop of $\text{K}_4\text{Fe}(\text{CN})_6$ solution on the paper almost simultaneously and the stop watch started at the same moment. The time in seconds till the observation of the blue colour was recorded and called "sizing value".

Chapter Three

R E S U L T S

Blank sheets of 2.12gms were observed to contain a mean quantity of about 0.4mg aluminium while the backwater samples obtained, contained about 1.5 and 1.1mg of aluminium and rosin respectively. These correcting factors were determined for each set of experiments and deducted from our experimental values.

The effectiveness of rosin as a sizing agent could be studied by determining the amounts of aluminium in the backwater and in the sheet and of rosin in the backwater when standard sheets were made at subsequent variation of alum and rosin quantities added to the pulp of pH 4.3.

Since the analysis of rosin in sheet was not successful, sizing values were determined. These values cannot be directly related to a figure for the amount of rosin present in the sheet, hence they cannot be used for a material balance. Nevertheless, these values are a useful representation of the effect of increasing rosin quantity in the sheet and as such of great value for the paper-maker as a quick assessment of the efficiency of a mill's sizing operations.

3.1 Variation of pH:

Resin in Backwater.

Determinations were carried out as described in chapter two at 255nm, using backwater samples collected when sheets were made at different pH values. The pulps were treated with 1.62 and 25µg of aluminium and rosin respectfully. The results are shown in Table 5 and Fig.14. A minimum was observed at about pH 4-4.5.

Aluminium in Backwater.

Samples obtained from above were extracted for their aluminium contents. It was observed that extraction in warm solvents produced a dark greenish coloration, but when solutions were cooled in ice the intense yellow coloured complexes of aluminium and quinoline were formed. Exposure to light also produced orange colorations instead of yellow hence absorbances should be read immediately after extraction. The results are shown in Table 5 and fig. 15. The graphs showed a plateau at about pH 4-4.5.

Aluminium in Sheets.

Weighed samples were ashed and the aluminium determined as in the experimental. The results (Table 6 and fig. 16) were corrected for the initial aluminium contents of the sheets. A similar plateau at about pH 4-4.5 was also observed.

Sizing value of the sheets.

Aqueous liquids as they penetrate paper, travel both in the vertical and horizontal planes. The times recorded for the rates of penetration as said in the experimentals might have been on the higher side. The non-uniformity of the hand-sheets made would also affect the time recorded, but in both cases when imported and local rosin were used maximum sizing values were observed at about pH 4-4.5 (See Table 6 and fig. 17).

The optimum sizing pH.

Lowest penetration rate should occur at the most effective sizing range; e.g. at pH 4-4.5 for both local and imported rosin. At this range also we observed a minimum in the rosin curve in backwater and plateaus for aluminium curves both in backwater and sheet. Within this pH range, pH 4.3 was chosen as our working pH.

3.2 Variation of rosin concentration:

In this case standard sheets were made as before but the pulp was treated with 10 mls of alum (0.2%) and various rosin concentrations. The pH of the pulp was adjusted to 4.3 and the following analysis were carried out as before.

Rosin in Backwater.

Determinations and corrections were carried out as before. The results are in Table 7 and fig. 18. The graph showed a gradual increase of rosin in backwater with a change in gradient when about 11.0 mg. local rosin was added while this was observed for imported rosin when about 12.5 mgs was added.

Aluminium in backwater.

The results are in Table 7 and fig. 19. The aluminium content of the backwater samples decreased asymptotically for both rosin samples. For the local rosin, the graph flattened out at about 10.0mg addition while it occurred at about 12.0 mg rosin addition for imported rosin.

Aluminium in Sheet.

The results for these determinations are recorded in Table 8 and fig. 20. A gradual increase was observed but in both cases the increase petered out. For imported rosin this point was observed after about 11.0 mgs of rosin was added and for local rosin after about 10.0mgs added.

Sizing values of the Sheets.

Similar curves were observed for both local and imported rosin. The curves showed a decrease in rate after

about 10.0mgs of rosin were added in both cases (See Table 8 and Fig. 21).

Optimum rosin concentration.

For imported rosin, additions after about 0.5% rosin per unit weight of oven dried pulp did not give any reasonable increase in sizing values. Also increases in rates of aluminium and rosin retentions were little. Additions in excess of 0.5% local rosin on a given pulp samples did not give corresponding increases in sizing values and retention of rosin and aluminium.

3.3 Variation of Alum concentration:

Sheets were made as above at pH 4.3 with 10 mls of stock rosin (25.0 mgs) while the alum concentration was varied.

Rosin in Backwater.

The rosin quantities in the backwater decreased rapidly and then remained constant in both cases. These flattened portions were observed after about 0.6 and 0.8 mg of aluminium were added when local and imported rosin were being used respectively (See Table 9 and Fig. 22).

Aluminium in Backwater.

There was an increase in the aluminium contents of the backwater samples until about 0.7mgs addition with local

rosin when the rate of increase suddenly increased rapidly and was parallel to that line drawn when no aluminium was retained by the sheets. Due to low experimental values, the rate decreased slightly for imported rosin but a change in gradient was observed after about 0.8mgs addition of aluminium (See Table 9 and Fig. 23).

Aluminium in Sheets.

The aluminium retention increased and then flattened out in both cases. The flattening occurred after about 0.7 and 0.8 mgs. of aluminium were added with local and imported rosin respectively (See Fig. 24 and Table 10).

Sizing values of the Sheets.

The results are shown in Table 10 and Fig. 25. For imported rosin the increase in sizing values was little after about 1.0mg of aluminium has been added and for local rosin after about 0.6mg of aluminium was added; but values were much lower than those observed for imported rosin.

Optimum aluminium concentration.

In our laboratory experiments, optimum sizing was achieved with 2.8% of aluminium in the case of local rosin where as 3.6% aluminium lead to optimum sizing with imported rosin (Percentages calculated on the weight of oven dried rosin). This is about 35% and 45% of alum sample respectively.

Tables of Result:

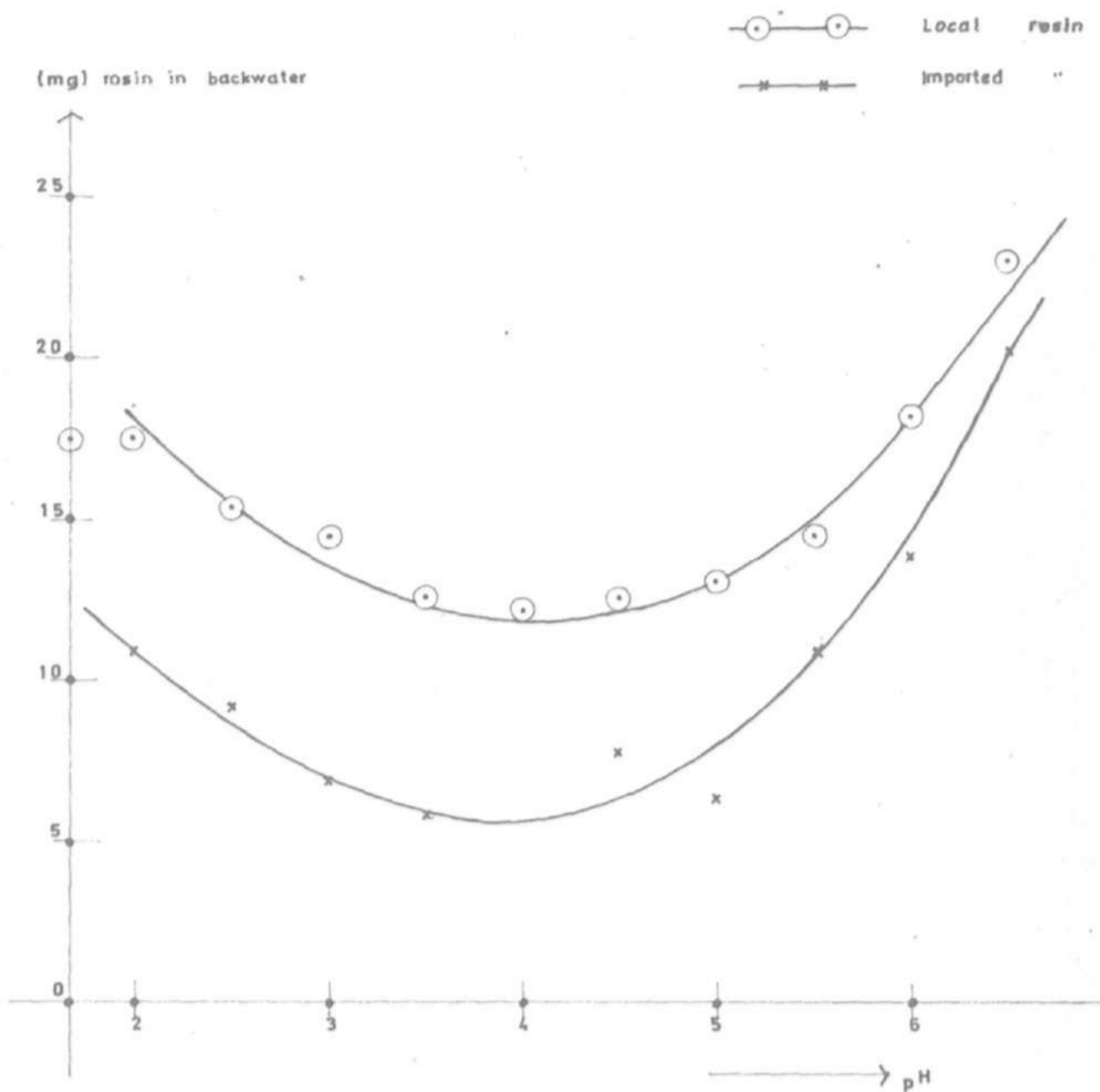
VARIATION OF pH

Table 5: Rosin and Aluminium in Backwater

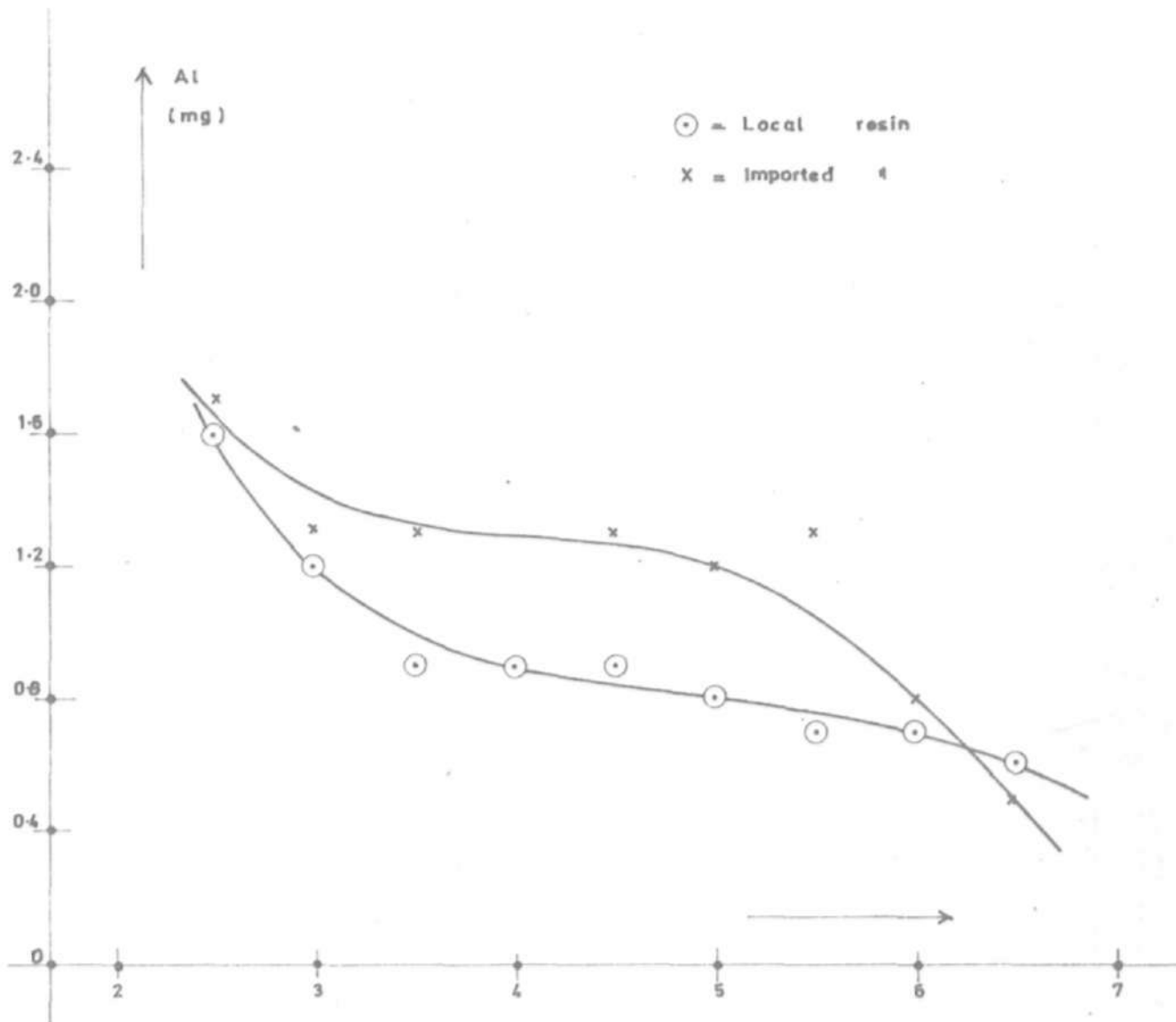
pH	Total rosin in Backwater (mg)		Total Aluminium in Backwater (mg)	
	Imported rosin	Local rosin	Imported rosin	Local rosin
2.0	10.9	17.5	2.1	-
2.5	9.3	15.4	1.7	1.6
3.0	6.9	14.5	1.3	1.2
3.5	6.0	12.7	1.3	0.9
4.0	11.6	12.2	2.2	0.9
4.5	8.6	12.6	1.3	0.9
5.0	6.3	13.1	1.2	0.8
5.5	10.9	14.5	1.3	0.7
6.0	13.9	18.3	0.8	0.7
6.5	20.1	21.2	0.5	0.6

Table 6: Rosin and Aluminium in Sheets

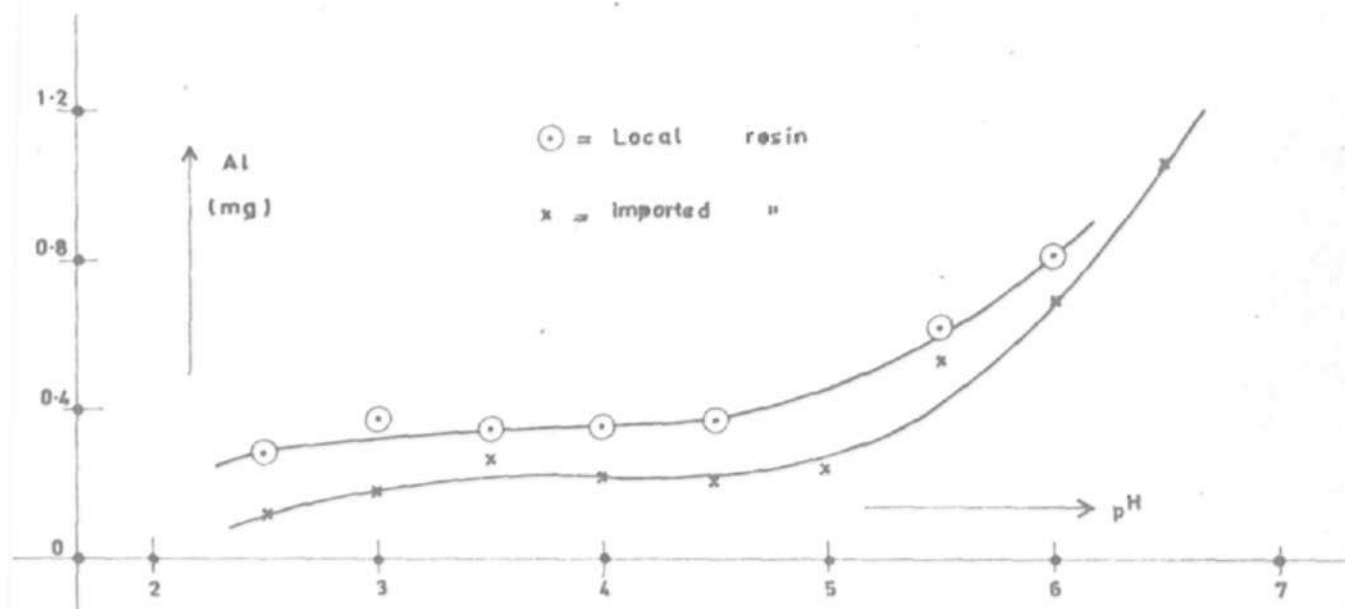
pH	Average sizing values (Seconds)		Total Aluminium in Sheets (mg)	
	Imported rosin	Local rosin	Imported rosin	Local rosin
2.0	< 2	-	-	-
2.5	240	< 2	0.1	0.3
3.0	625	24	0.2	0.4
3.5	518	260	0.3	0.4
4.0	944	368	0.2	0.4
4.5	941	450	0.2	0.4
5.0	646	443	0.2	-
5.5	603	391	0.5	0.6
6.0	497	311	0.7	0.8
6.5	415	225	1.1	-



GRAPH 5... TOTAL ROSIN IN BACKWATER (TABLE...5...)

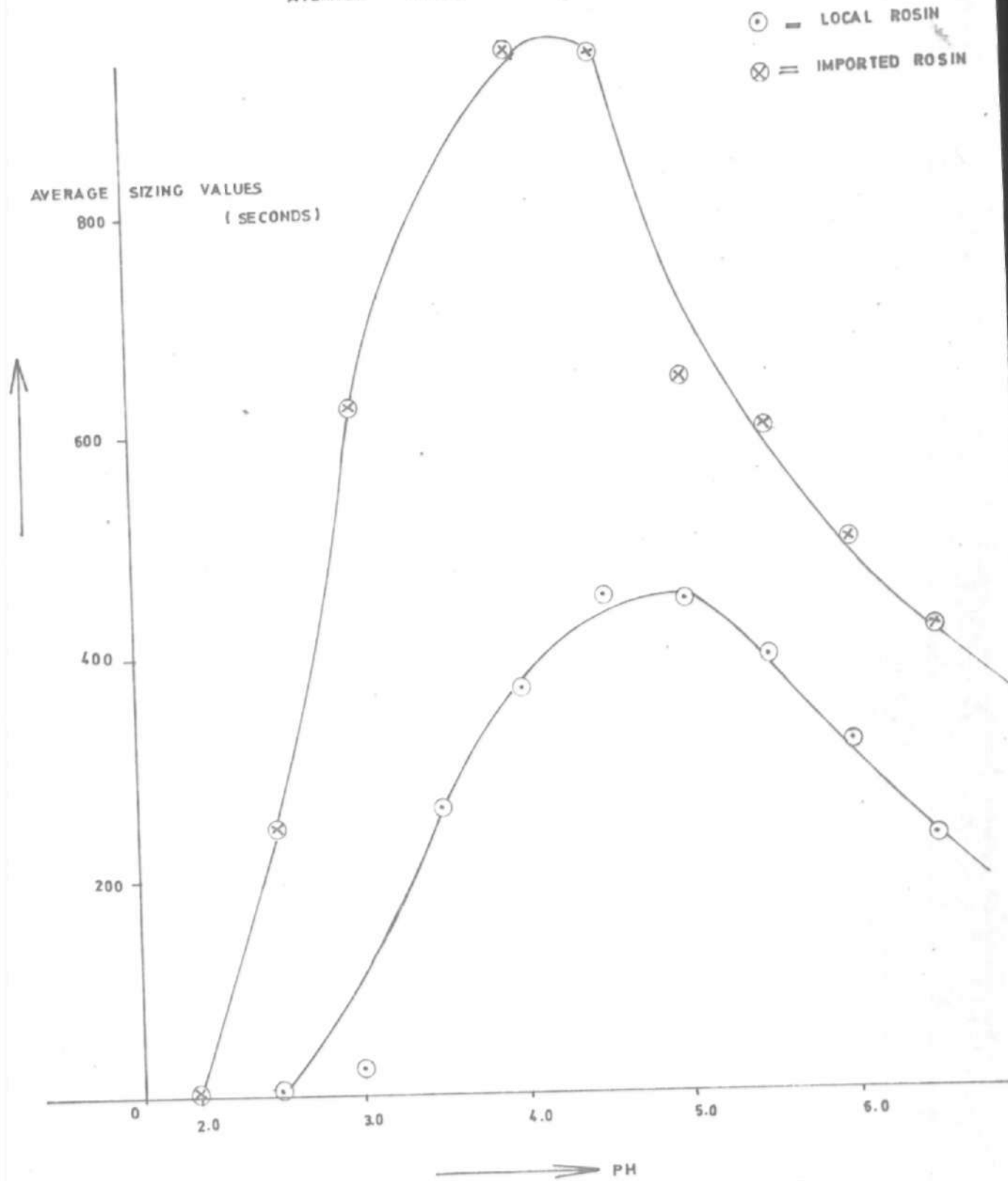


GRAPH 6... TOTAL ALUMINIUM IN BACKWATER (TABLE 5...)



GRAPH... TOTAL ALUMINIUM IN SHEETS (TABLE.. 6...)

AVERAGE SIZING VALUES ; Fig 17



GRAPH 8 AVERAGE SIZING VALUES TABLE 6

VARIATION OF ROSIN CONCENTRATION

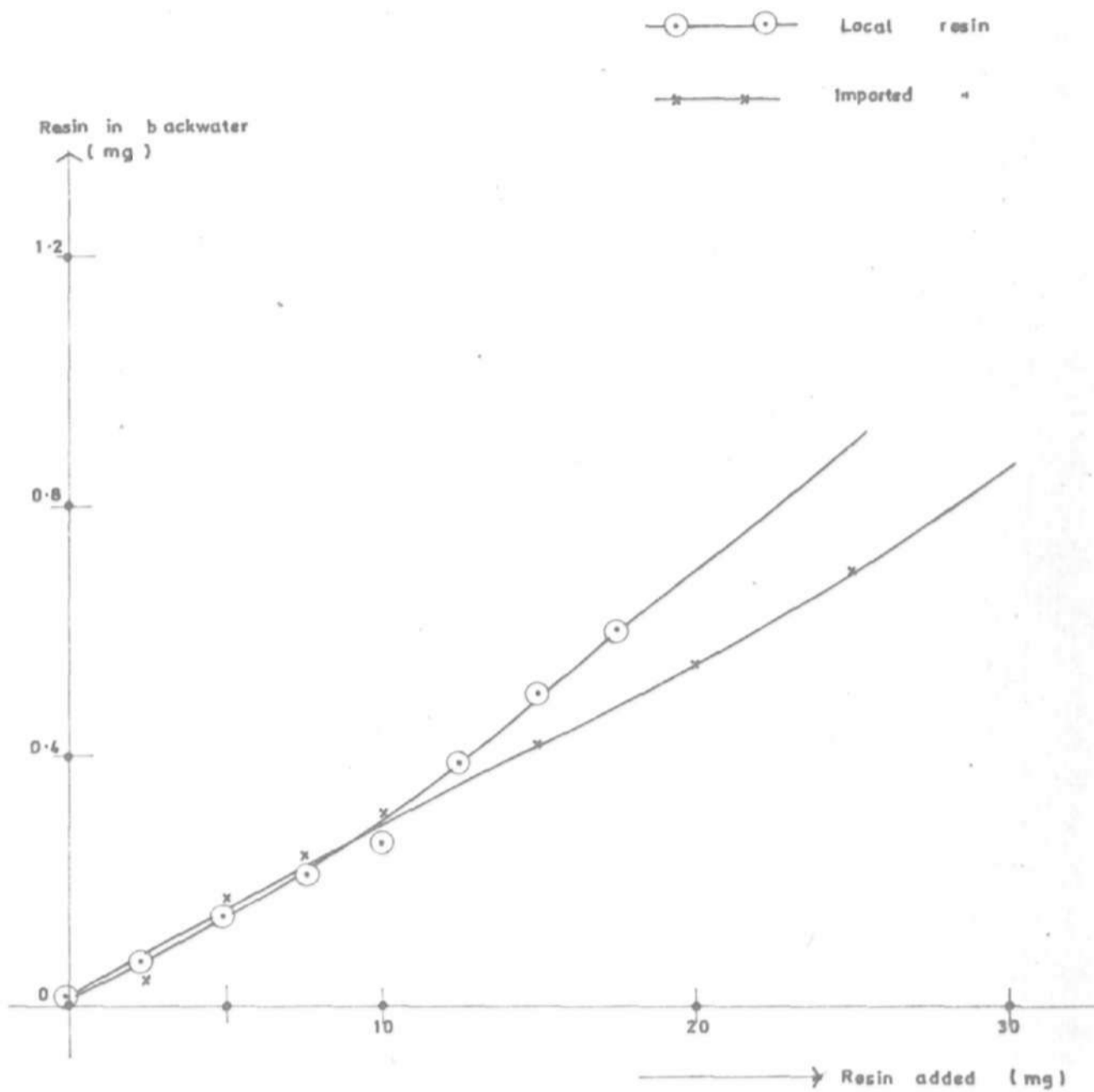
Table 7: Rosin and Aluminium in Backwater

Rosin added (mg)	Total rosin in Backwater (mg)		Total Aluminium in Backwater (mg)	
	Imported rosin	Local rosin	Imported rosin	Local rosin
0.0	0.0	0.0	1.7	1.8
2.5	0.4	0.7	1.1	1.1
5.0	1.7	1.5	0.6	1.1
7.5	2.4	2.1	0.5	1.0
10.0	3.1	2.6	0.5	0.8
12.5	-	3.9	-	1.0
15.0	4.2	5.0	0.5	1.0
17.5	-	6.0	-	1.0
20.0	5.4	-	0.5	-
25.0	6.9	-	0.5	-

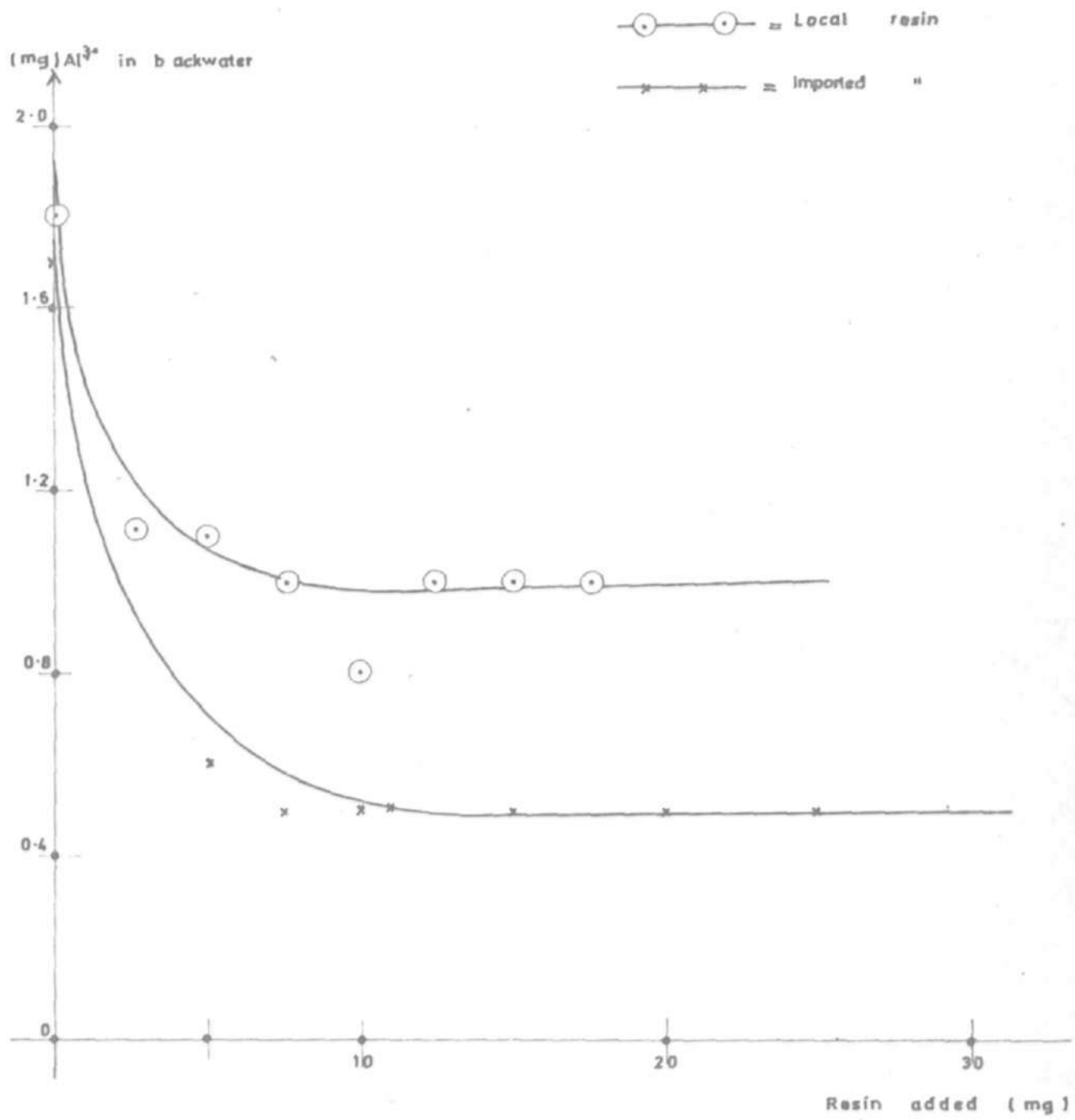
Table 8: Rosin and Aluminium in Sheets

Rosin added (mg)	Average sizing values (Seconds)		Total Aluminium in Sheet (mg)	
	Imported rosin	Local rosin	Imported rosin	Local rosin
0.0	< 4	< 2	0.1	0.2
2.5	31	8	0.4	0.3
5.0	180	94	0.5	0.4
7.5	401	281	0.6	0.5
10.0	474	533	0.6	-
12.5	-	517	-	0.5
15.0	500	535	0.6	0.5
17.5	-	548	0.6	-
20.0	546	-	0.6	-
25.0	582	-	-	0.5

ROSIN IN BACKWATER; Fig 18.

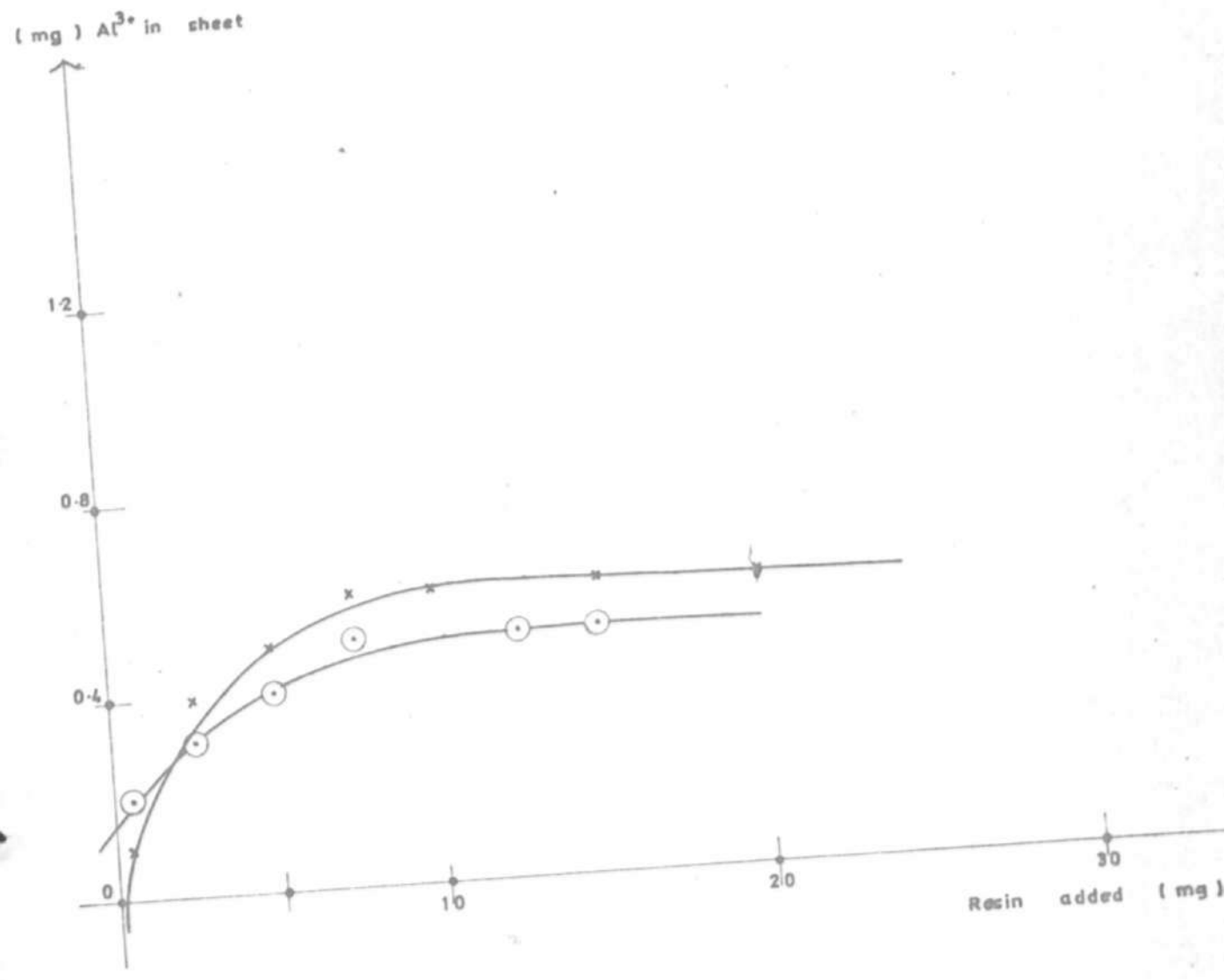


GRAPH 9... ROSIN IN BACKWATER (TABLE 7...)



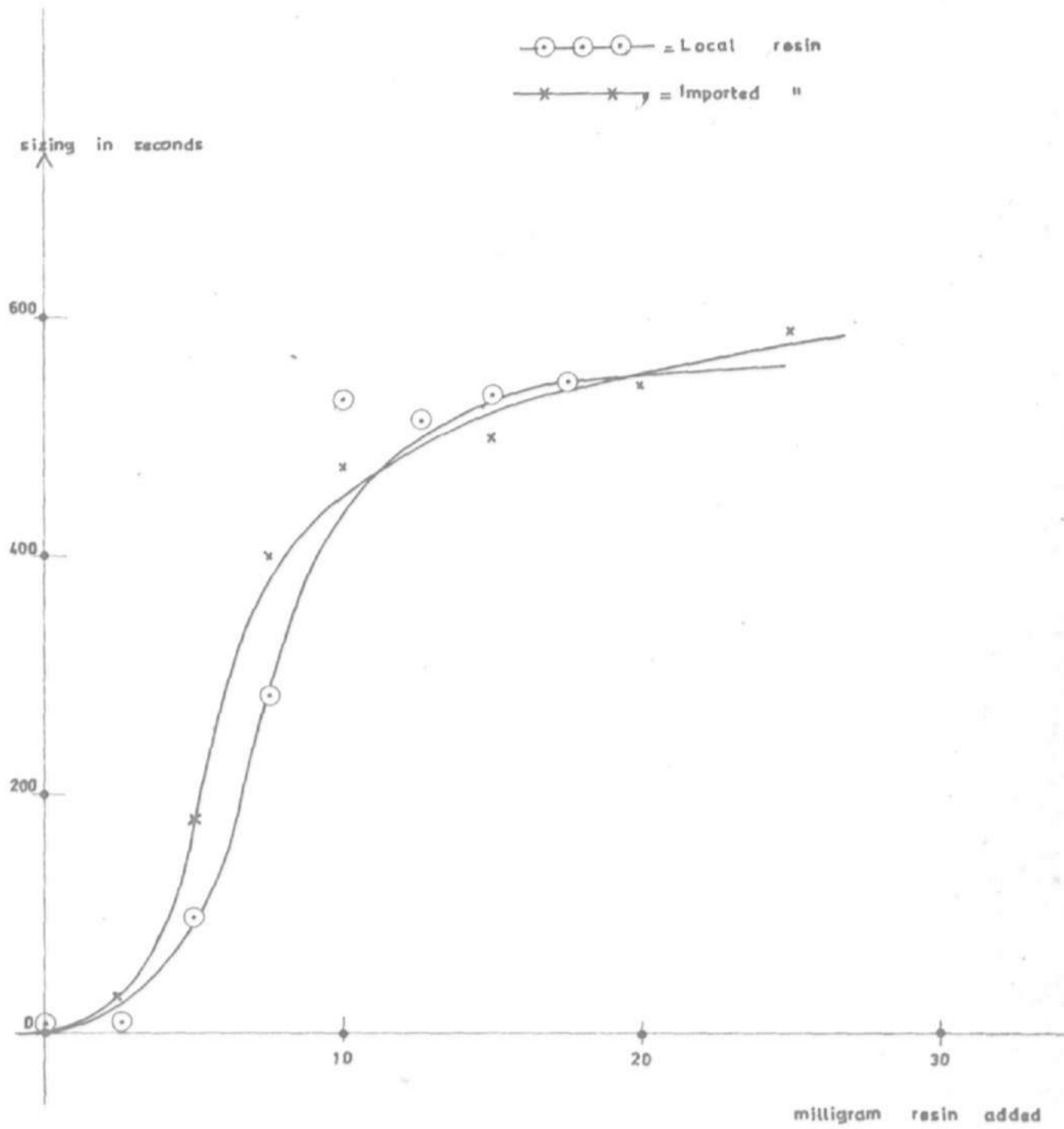
GRAPH 10... ALUMINIUM IN BACKWATER (TABLE 7.....)

○—○ = Local resin
x—x = Imported "



GRAPH... [ALUMINIUM IN SHEET TABLE ... 8.]

AVERAGE SIZING VALUES ; Fig 21.



GRAPH 12... (AVERAGE SIZING VALUES TABLE...g..)

VARIATION OF ALUMINIUM CONCENTRATION

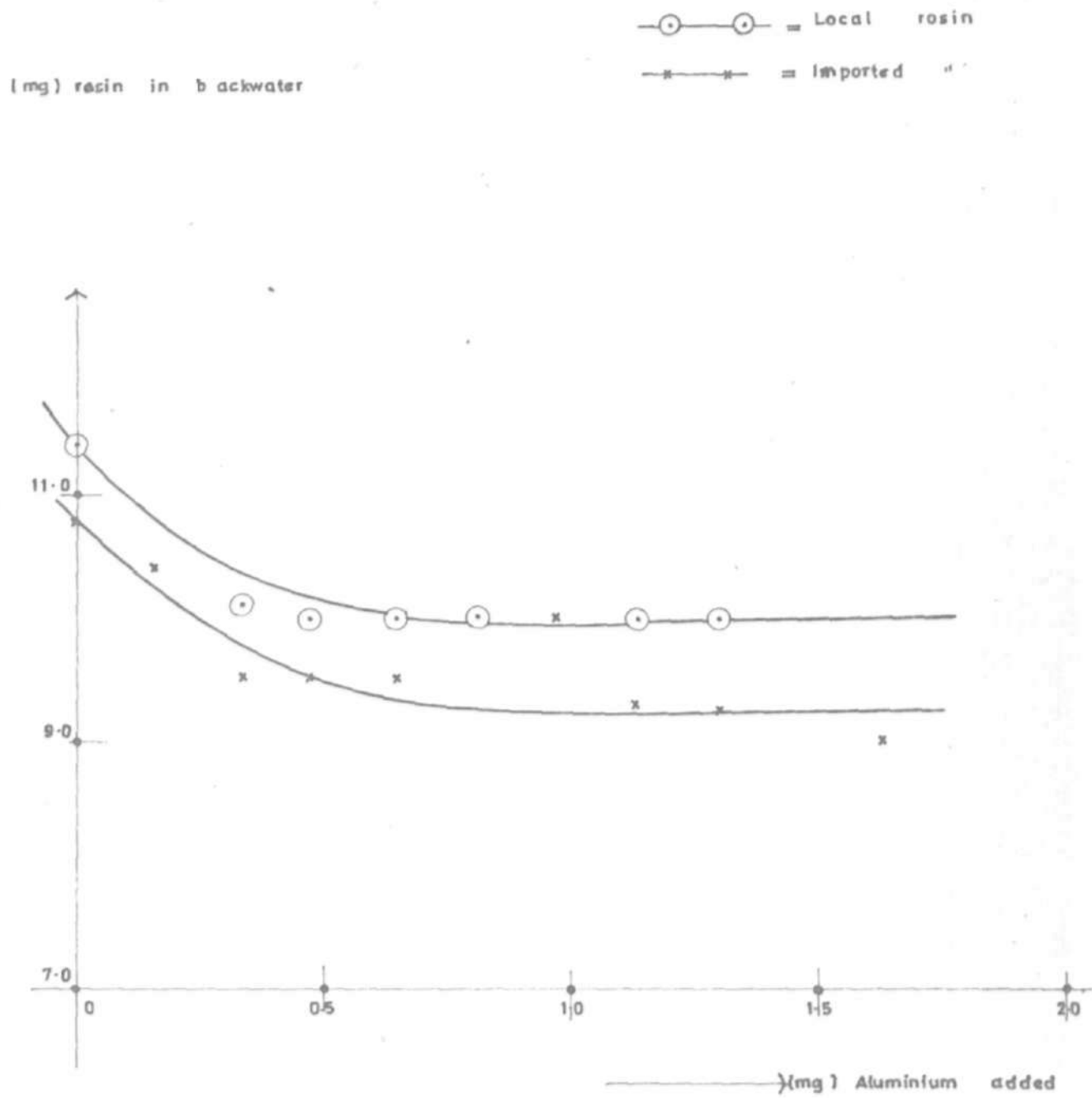
Table 9: Rosin and Aluminium in Backwater

Aluminium added (mg)	Total rosin in Backwater (mg)		Total Aluminium in Backwater (mg)	
	Imported rosin	Local rosin	Imported rosin	Local rosin
0.0	10.8	11.4	0.0	0.0
0.16	10.4	8.4	0.1	0.1
0.33	9.5	10.1	0.2	0.2
0.49	9.5	10.0	0.4	0.3
0.65	9.5	10.0	0.4	0.4
0.81	-	10.0	-	0.5
0.97	10.0	10.0	0.6	0.5
1.14	9.3	10.0	-	0.8
1.30	9.3	-	0.7	1.0
1.62	9.0	-	0.8	-

Table 10: Rosin and Aluminium in Sheets

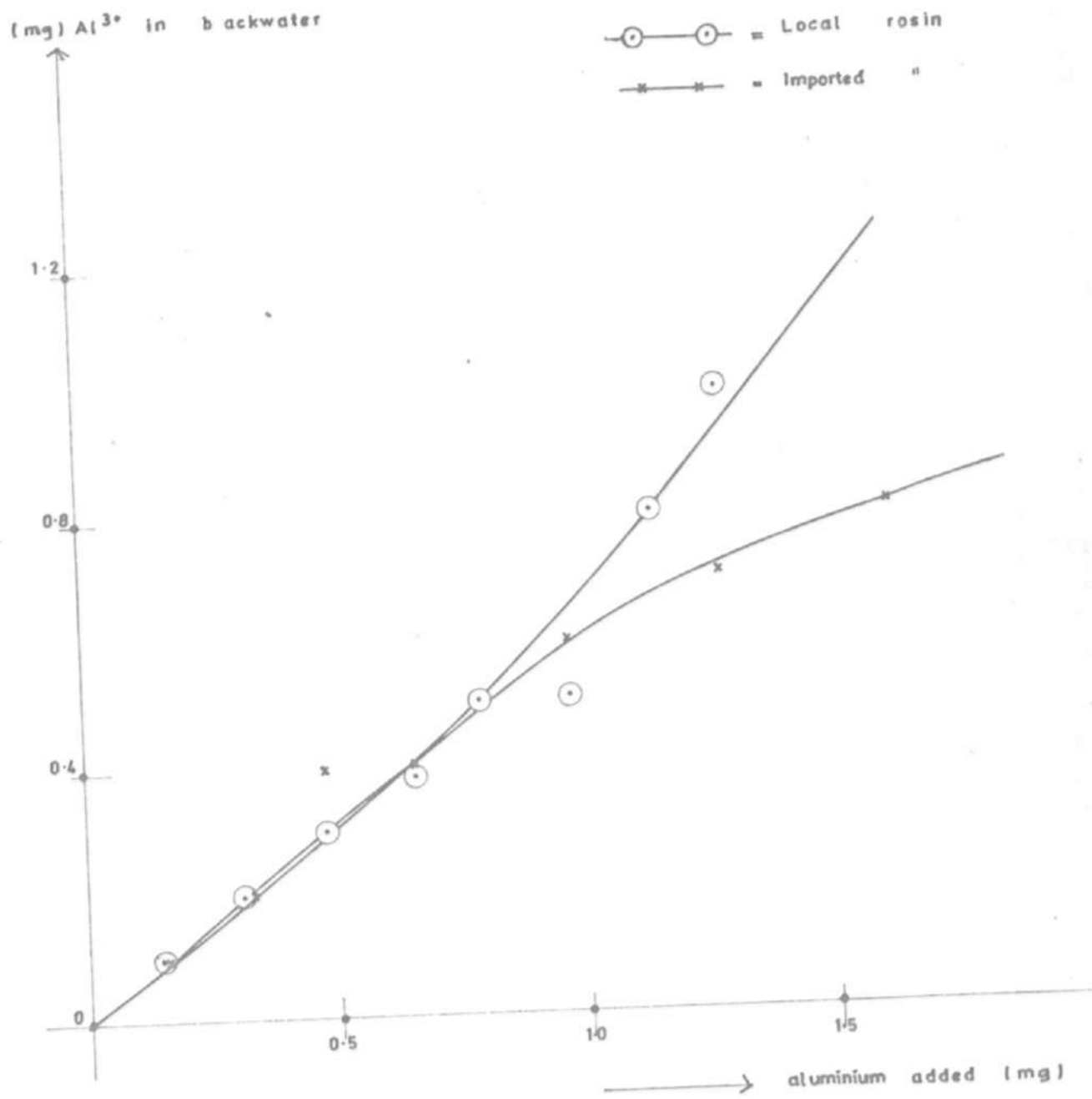
Aluminium added (mg)	Average sizing (Seconds)		Total Aluminium in Sheet (mg)	
	Imported rosin	Local rosin	Imported rosin	Local rosin
0.0	< 3	< 5	0.0	0.0
0.16	80	12	0.1	0.1
0.33	77	20	0.2	0.2
0.49	277	140	0.3	0.2
0.65	321	155	0.3	0.3
0.81	-	165	-	0.3
0.97	428	160	0.4	0.3
1.14	-	166	-	0.3
1.30	511	-	0.4	-
1.62	540	-	0.4	-

ROSIN IN BACKWATER; Fig 22.



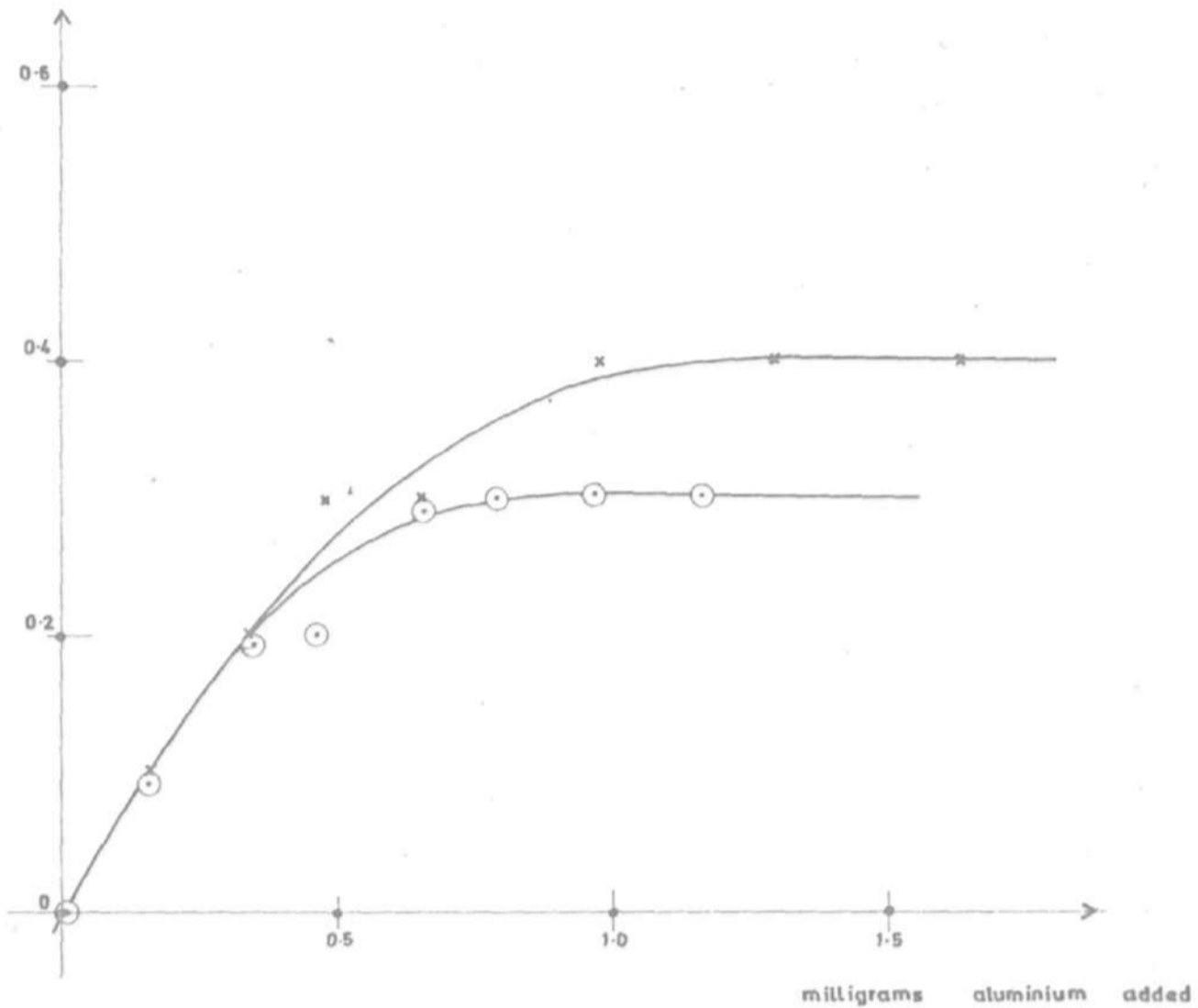
GRAPH 13... (ROSIN IN BACKWATER TABLE...9.)

ALUMINIUM IN BACKWATER ; Fig 23.



GRAPH..(4... (ALUMINIUM IN BACKWATER TABLE..9.)

milligrams Al in sheet



GRAPH 15... (ALUMINIUM IN SHEET TABLE... 10...)

Chapter Four

D I S C U S S I O N

4.1 Retention of Aluminium and Rosin as a Function of pH:

According to Ekwall²⁵, Guide²⁶ and Strazdins³, a major role in the sizing process is played by the products of the hydrolysis of the hydrated aluminium complex as mentioned in the introduction.

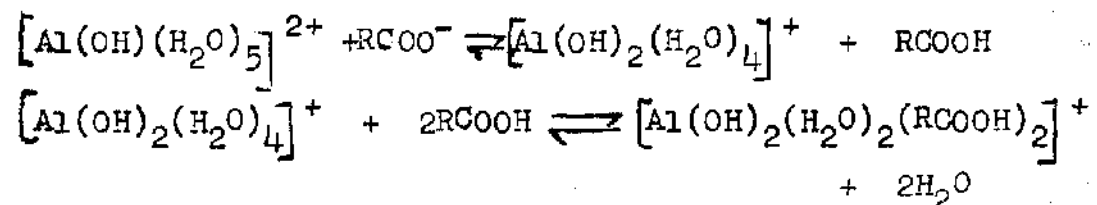
In 1965 Strazdins⁶ did some work on electromobility of the aluminium complexes precipitated from aluminium sulphate solutions at increasing amounts of sodium hydroxide. The results showed that the mobility is constant till about 2.5 equivalents of the alkali were added, then the mobility dropped sharply to zero when neutral $\text{Al}(\text{OH})_3$ flocs were produced. These observations were explained in-terms of changes in the surface charge of the complexes precipitated.

Millar²⁷, Reynolds and Linche³ showed that the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio was also constant till about 2.5 equivalents of alkali added.

The above facts indicated that as neutralization proceeded, all the aluminium ions were converted into the first products of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ hydrolysis - ($[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$).

When all the aluminium hydrates have been converted into the monohydroxylated products, further addition of alkali converted these again into di-hydroxylated complexes (i.e. $[\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4]^+$ with less positive surface charge hence mobility decreased. The hydrolysis is repeated till neutral $\text{Al}(\text{OH})_3$ flocs were formed.

Our results at varying pH values could be explained using the above facts. At low pH values, only a few monohydroxylated ($[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$) complexes were formed and the amount available was quickly consumed by the rosin added to give the sizing complex indicated in the introduction. - i.e.;



The diresinate formed is attracted to the negatively charged cellulose fibres. At low pH the trivalent hydrated aluminium complexes ($[\text{Al}(\text{H}_2\text{O})_6]^{3+}$) also compete with the diresinates for attachment onto the fibres. When this happens, the negative charges on cellulose are quickly neutralized and the cellulose may even acquire a net positive charge and repel the positively charged diresinates.

This means low retention of sizing complexes (diresinates) at low pH values. This is shown by the large amounts of rosin and aluminium present in the backwater (Figs. 14 and 15).

As the pH value increases, most of the trivalent hydrated aluminium ions are converted to monohydroxylated complexes. These react with more rosin to give more of the Al/Rosin sizing complexes which are retained by the fibres. This means an increase in retention of both aluminium and rosin and a corresponding decrease in the amounts detected in backwater (Figs. 14, 15 and 16).

For rosin in backwater, a minimum^m is observed at about pH 4-4.5. This point corresponds to maximum retention (Fig. 14). Graphs of aluminium estimated (Figs 15 and 16) showed that increases of aluminium in the sheet and decreases in backwater diminished, to give an area of constant value. This is within pH 4-4.5 and it supports the assumption that the minimum observed for the rosin in backwater corresponds to the range of maximum rosin/aluminium complex adsorption. This saturation phenomenon agrees with the fact that the sizing theory postulates attachment of sizing complexes to individual negatively charged sites on cellulose. Once these sites are used up, there is no more increase in aluminium or rosin retention

since no more sizing complexes can be absorbed.

Above pH 4-4.5, there is a sharp rise in rosin quantity determined in backwater (Fig. 14). A corresponding increase for aluminium in sheets and a decrease for aluminium in backwater were observed. (Figs. 15 and 16). This could be explained by the fact that at higher pH values, excess $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ were formed. These compete with the diresinate sizing complex, hence less rosin but more aluminium was retained by the fibres. Excessive absorption of $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ by the fibres result in a nett positive charge build up and the Al/Rosin sizing complexes are repelled by the fibres. This also reduces the retention of aluminium and rosin.

Strazdins³ observed that the free rosin acids, unsaponified during cooking of rosin, contribute to the reduction in retention. This is because at high pH values, the free acids ionize to give RCOO^- that can react in competition with the negative sites not occupied, for fixation onto the positively charged substances present (including Al/Rosin sizing complex and other positively charged hydrolysis products).

He also observed that up to pH 8-9, positively charged aluminium ions are still present in solution; as a consequence some types of Al/Rosin complexes not contributing

to the sizing could be present in the whole pH range studied.

Our study of the sizing values at various pH values showed that the values increased with pH to maximum at about pH 4-4.5 followed by a rapid fall from pH 4.5-5.3. A more gradual fall followed from there on. (Fig. 17).

An explanation based on theory of sizing is that there is an increase in Al/Rosin sizing complex retained, hence the sizing values increase. At the maximum sizing value we have the maximum retention of Al/Rosin sizing complex.

In previous paragraphs, it was indicated that less rosin was retained at high pH, though more aluminium was retained, due to excessive $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ formation. This will explain the sharp fall in sizing values. The slower fall from pH 5.3-6 may be due to the moderating effects of the ionized free rosin acids as mentioned earlier. These RCOO^- radicals react in competition with the negatively charged sites on fibres for the excess $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ formed. This allows more sizing complex to be retained leading to higher sizing values in the alkaline pH range than in very acidic pH range. The result is that generally some sizing effects are still

possible at alkaline pH values. However a drop in pH towards the extreme acid region causes a complete loss of sizing.

4.2 Retention of Rosin and Aluminium as a function of Rosin concentration at pH 4.3:

Direct estimation of rosin in sheet was not successful but sizing values which are indications of the amounts of rosin present in sheet were determined.

In Fig. 18 we see that the rosin found in backwater increased almost linearly with increase in rosin added. When about 11.0mg (for both local and imported rosin) were added a change in gradient upwards was observed. This is about 0.5% of rosin on oven dried weight of a given pulp sample.

An explanation could be that at the point of change in gradient, the fibres were saturated. The graph after that point is almost parallel to the line obtained when no rosin is retained by the fibres.

Estimations of aluminium quantities in backwater (Fig. 19) agreed with the above observations since when no rosin was added, none or little aluminium was retained so most came down in the backwater (about 1.7 and 1.8mg aluminium found for imported and local rosin respectively).

With increase in rosin quantities, more and more Al/Rosin sizing complexes are formed hence the aluminium retention (Fig. 20) increased whereas less aluminium was detected in backwater (Fig. 19). Above a rosin addition of 11mg, a constant amount of aluminium was observed in water and in sheet indicating a saturation of the fibres with Rosin/Aluminium complex.

Sizing curves (Fig. 21) showed an increase with addition of rosin till an optimum quantity of 11mg was added.

At the optimum rosin dosage, about 0.6 and 0.5mg of aluminium in sheet were observed for both imported and local rosin. This corresponds to about 6% and 5% on oven dried weight of rosin used at that point.

4.3 Retention of Rosin and Aluminium as a function of Aluminium concentration at pH 4.3:

As said in the introduction, maximum sizing effects with rosin are observed in the presence of precipitating agents like aluminium ions.

With increase in aluminium concentration in pulp, the graphs of aluminium found in backwater were analogous to those obtained for rosin determined in backwater at various rosin concentrations. (Figs. 23, 18). The characteristic change in gradient was observed when about 0.8mg of aluminium was added.

The aluminium quantity retained in the sheet increased rapidly with the amount of aluminium added to a constant value when about 0.8mg of aluminium was added (Fig. 24).

Rosin in backwater showed a corresponding rapid decrease till about 0.8mg of aluminium was added; then amounts detected remained constant (Fig. 22).

Corresponding to these observations, the sizing values showed an increase but after the optimum aluminium addition the increments were very small per unit amount of aluminium added. (Fig. 25). Initially the values scattered as shown by the broken lines. This could be due to an uneven distribution of the first few sizing complexes formed. When enough sizing complexes were formed, distribution became uniform and points were less scattered.

These results were explained along the same lines as in the rosin concentration experiments. With increase in aluminium quantities in the pulp slurry, more Al/Rosin sizing complexes were formed hence retention and sizing values increased till the fibres were saturated.

4.4 Comparison of Local and Imported Rosin:

A study of the graphs of rosin determined in backwater under various experimental conditions (Figs 14, 18, and 22) showed that more local rosin was detected than

imported rosin. At optimum pH value, rosin concentration, and aluminium concentration, about 46%, 27%, and 40% of the local rosin added were detected in the backwater respectively. Corresponding values for imported rosin were 22%, 27% and 37% of the amounts of rosin added respectively.

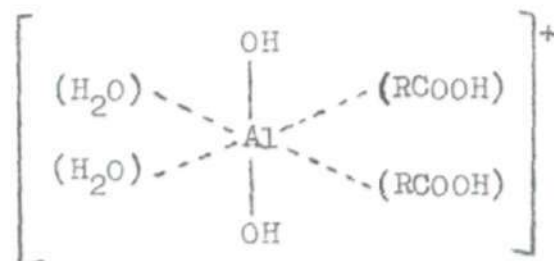
Results of aluminium determinations in backwater (Figs. 19, 23) showed higher values for local rosin than for imported rosin. At optimum addition of local rosin 60% of the aluminium added was found in the backwater. With imported rosin the corresponding value was 31%. At optimum addition of aluminium 63% of the aluminium added with local or imported rosin was detected for both. In the sheets 38% of the aluminium added was detected at the optimum imported rosin addition while 31% was found with the optimum addition of local rosin. Similarly at the optimum aluminium concentration, retentions of aluminium were about 50% and 38% respectively.

In two of the three sets of experiments, the sizing values with imported rosin were substantially higher than with local rosin. This was not obvious from the sizing results obtained with rosin concentration variation (Figs. 17 and 25). However in the other two series of

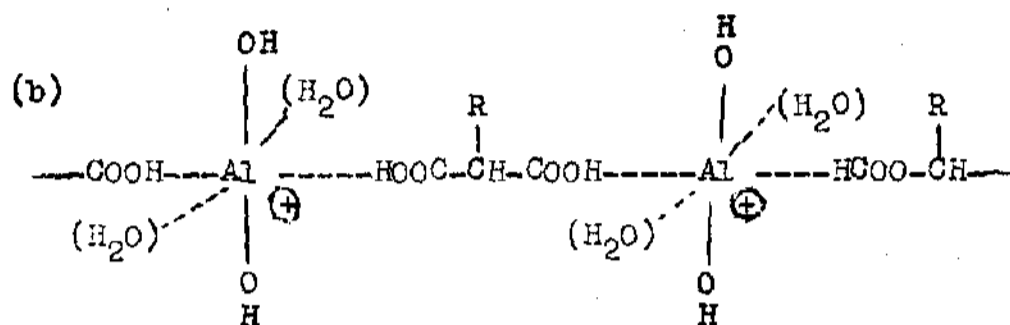
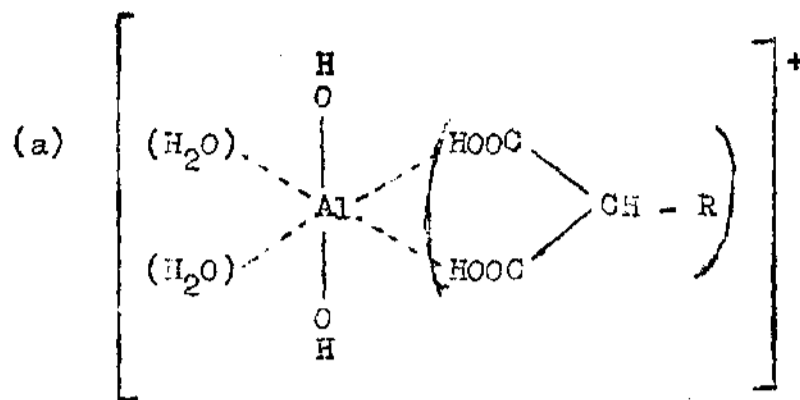
experiments, imported rosin gave values that were about twice as large as those of local rosin (Figs. 17 and 25).

It can be concluded that in our experiments the retention of the imported rosin sample is better than that of the locally collected rosin, leading to higher sizing values with imported rosin.

A tentative explanation could be found in the structures of the two rosin samples. It is known that abietic acid and its isomers possess only one functional group (the $-\text{COOH}$), and all their sizing reactions are due to this group. Assuming that imported rosin also contain only one functional ^{group} per molecule, the structure of the sizing complex as a diresinate can be written as



It is possible that on the average the local rosin contains more than one functional group per molecule, which could be $-\text{COOH}$ groups or others. In the case of two $-\text{COOH}$ groups, the complex can be written as structure (a) shown on the next page. However a chain structure (b) is also possible.



In the two structures last mentioned, monoresinates were formed. Gray and Alexander²⁸ showed in their studies on sizing with aluminium stearates that only di-stearate is an effective sizing agent, and not the monostearate. If the same holds for diresinate and monoresinate, then the observed differences between imported and local rosin could be explained accordingly.

Another explanation could be that impurities forming non-sizing Al- complexes were present in the local rosin sample. These complexes could also be retained by the

fibres since they would be positively charged. This will reduce the amount of local rosin retained in the sheet hence large amounts detected in backwater. This will give low sizing values when compared with imported rosin.

This explanation finds some support in the values of the routine analysis of the two samples. However these differences appear to be too small to explain the observed differences in behaviour in our experiments. (See pages 17-18).

Chapter Five

C O N C L U S I O N

Determinations of the retention of aluminium and rosin as a function of pH showed that sizing effect is dependent on the amount of rosin that could be retained by the cellulose fibres.

The formation of the sizing complex and its retention is dependent upon a number of factors. The pH of the sizing system profoundly affect this complex formation as indicated in chapters one and four. With increase in the sizing complex retention, the sizing values increased. The optimum pH for the formation and retention of the sizing complexes was found to be in the range of 4.0-4.5. The maximum retention in the fibres was indicated by the shape of the graphs of aluminium in the sheets and in backwater.

A tentative conclusion is that a partial saponification of rosin leaving some free rosin acid present in the "Cook" can enhance the sizing ability of the rosin soap emulsion used in paper mills. A probable mechanism

has been described in the previous chapter.

Lastly it has been shown that the aluminium retention is high around pH 5.0-6.5. This is in agreement with Strazdins statement that positively charged aluminium species are present through^{out} the pH range we studied.

Results obtained when rosin concentration was varied at pH 4.3 showed that with increase in the amounts of rosin added the aluminium detected in sheet increase. The cellulose fibres will continue to adsorb the sizing complexes until a saturation state is reached corresponding with a constant value in the aluminium content of backwater samples and in the sheets. Saturation was observed at about 11mg rosin addition. This is about 0.5% on oven dried weight of the pulp sample used. Addition of rosin above 0.5% gave very little increase in retention of rosin and alum.

These observations are supported by the sizing values obtained (Fig. 21). The practice in mills is to add about 1-1.5% rosin to a given weight of oven dried pulp (giving allowance for the degree of efficiency of mill operations and for losses). It is known that excessive rosin addition can cause a loss in the quality of the paper produced in the mill.

Varying the aluminium concentration in the pulp slurry at pH 4.3, similar results as above were observed. Sizing values will improve with increases in the quantity of aluminium added till a state of saturation is reached.

Saturation was observed when about 3.5% of aluminium on oven dried weight of rosin was added. (40% alum).

Finally it appears that our sample of imported rosin gave better sizing effects than locally collected rosin. Tentative explanations for this observation have been mentioned in chapter four.

R E F E R E N C E S

1. Britt, K. W. "Handbook of Pulp and Paper Technology".
Second Edition. pp.327-395. Van Nostrand
Reinhold Company - New York (1970).
2. Verhoeff, J. and Gallay, W. Pulp and Paper Magazine
of Canada. T509-511, (1963).
3. Strazdins, E. Tappi. 46, 432-437, (1963).
4. Watkins, S.H., Tappi 45, 216, (1962).
5. Britt, K. W., "Handbook of Pulp and Paper Technology"
Second Edition pp.360-361, Von Nostrand Reinhold
Co., New York (1970).
6. Strazdins, E., Tappi 48, 157-164, (1965).
7. Davidson, R. W.; Tappi 47, 609, (1964).
8. Kent, J. A., "Industrial Chemistry". Fourth
Printing pp.592-600, Van Nostrand Reinhold,
New York, (1968).
9. Iyambo, D. E; and Jackson, J. K; Research Paper
(Savannah Series) No. 2, (1972).
10. Ojo, G. O; and Shadow, M. B; Research Paper (Savannah
Series) No.19. (1973).
11. Norris-Shrave, R., "Chemical Process Industries"
Second Edition pp.713-717, McGraw-Hill Co. (1956).
12. "Internal Sizing of Paper and Paperboard"
Tappi Monograph Series No.33, pp.12-15.
13. George, C.H; and Sanderson, T. F., Journal of
American Chemical Society, 70, pp.334-339, (1948).
14. Newell Stephenson, J., "Pulp and Paper Manufacture"
Vol.II Revised Edition of Vol. IV pp.240-302
McGraw-Hill Book Co. Inc. London (1951).

15. Britt, K.W; "Handbook of Pulp and Paper Technology"
Second Edition pp.665-670, Van Nostrand
Reinhold Co. - New York (1970).
16. Kama-Pa-Gikyoshii - Japan 22, 140-146, (1968).
17. Kirk and Othmer; "Encyclopaedia of Chemical
Technology", Second Edition Vol.17, p.490.
Interscience Publishers, New York, (1971).
18. Chemical abstract (1833-8), (1924).
19. Wise, L.E. and Jahn, E.C. "Wood Chemistry". Second
Edition. Monograph Series No.97, pp.447-500.
Reinhold Publishing Corp. New York, (1952).
20. Williams, H.D. and Fleming, I; "Spectroscopic methods in
Organic Chemistry", p.24, McGraw-Hill Pub. Co.
Ltd., London (1966).
21. Vogel, A.I., "Qualitative Inorganic Analysis"
3rd Edition, pp.400-800. Longmans Green and Co.,
Ltd., London, (1961). pp 457, 472, 792
22. Kolthoff, I.M. and Sandell, E.B., "Textbook of
Quantitative Inorganic Analysis", 3rd Edition
p.319, The Mcmillan Co. - New York, (1952).
23. Blum, W., Journal of American Chemical Society"
38, p.1282, (1916).
24. Burke, E.K., Analytical Chemistry, 38, pp.1608-1611
(1966).
25. Ekwall, P. and Brunn, H.H.; Tappi 37, pp.303-6, (1954).
26. Guide, R. G. Tappi 42, p.734, (1959).
27. Miller, L.B.; Technical Association Papers, 22, p.141
(1939).
28. Gray and Alexander - Tappi Monograph Series
Internal Sizing of paper and Paperboard No.33
p.147.