OPTIMISATION OF COMMERCIAL PRODUCTION PROCESSES FOR POLYESTER RESINS

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SUMMARY

This thesis describes the work undertaken for the Teaching Company organised between BIP Chemicals Ltd and the University of Aston, Department of Chemical Engineering and Applied Chemistry. The overall aim of the scheme was to examine the process parameters involved in commercial polyester production and recommend new procedures to ensure both consistent process operations and product quality. The specific reactions involved in the preparation of polyester resins are discussed along with commercial manufacturing methods. The traditional quality control testing methods are described in order to compare with the techniques developed in the Teaching Company, ie new control tests to determine the solids and ash content of polyesters. The result has been a significant reduction in test time and improved reproducibility of measurement. Therefore, hold-ups associated with awaiting results are reduced, thus increasing plant availability, resulting in a potential increase in production equivalent to £652,548 pa additional contribution. The data are recorded to a higher degree of accuracy than is achievable by the standard test method, providing a firm basis on which to measure improved product quality.

The installation of a mass flowmeter into the distillate line of one reactor has provided an additional control parameter, ie the water removed from reaction can be measured, thus providing a better understanding of the course of the reaction and control of the overhead equipment.

Optimisation of existing equipment, such as an ultrasonic homogeniser and the cooling water flow rates to the overhead equipment, have further improved productivity by 37% on one of the smaller reactors.

The research work has been highly successful, with new control strategies and new test methods improving productivity and hence providing the potential for large financial returns.

Key words

Quality Control Testing
Solids and ash content by microwave drying
Free glycols in polyester resins
Process operating instructions

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CHAPTER 1

INTRODUCTION

1 INTRODUCTION

The work reported in this thesis reflects part of the project examined by the Second Teaching Company set up between BIP Chemicals Ltd and the University of Aston in Birmingham. The overall aim of the scheme was to examine the process parameters involved in commercial polyester production and identify suitable parameters for process control to produce both consistent process operations and ultimately a more consistent product. Other areas of interest studied included development of chemical analytical techniques for polyester resins:

ie (i) new techniques for in-process testing

(ii) a suitable technique to relate the rheological properties of polyester resins to their glycol content

and the relationship between the chosen control parameters and the end-use of polyester resins. There were two Research Associates involved in the scheme, working together to develop an improved batch control strategy. The outcome of the work was highly successful, with the implementation of new equipment/procedures and analytical techniques providing improved process control.

The type of resin under investigation is a polyester resin and is used in a variety of applications, eg the marine, transport and building industries are the major users of polyesters, but many other industries, such as the paint industry, also find use for polyesters.

BIP manufacture over eighty different polyester resins. However, many are variants of the basic polyester resin, so the production plant under consideration is a typical multiproduct, batch plant. The reactors are manually operated, as a result of which both the process and product quality can be variable and from time to time batches fall outside the specification limits, thus necessitating expensive rework procedures or the costly loss of a complete batch.

The object of this work was to investigate the control parameters used in the batchwise production of polyester resins. This involved examination of the existing process to determine exactly what was being measured by the present process control parameters and what were the important stages within the process. Once established, new control parameters and new/improved ways of measuring the existing ones were investigated to optimise process control. The possible introduction of new techniques for in-process testing, was examined by comparing suitable methods with the standard ones. In addition, the techniques required to examine polyester and its unreacted glycol content were researched. When complete, improved process control and the introduction of new analytical techniques will help to provide consistent process operations and improved product control.

CHAPTER 2

PROCESS CHEMISTRY

2 PROCESS CHEMISTRY

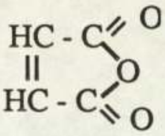
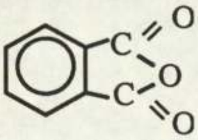
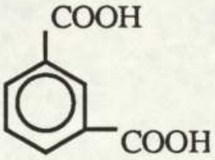
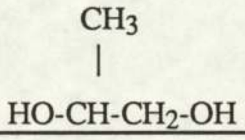
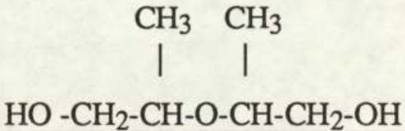
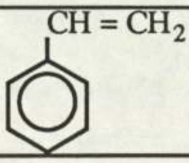
2.1 Introduction

Polyester resins are formed by the reaction of an organic dibasic acid with a dihydric alcohol (glycol). The nature and ratio of these reactants will determine the final properties of the resin. The main reactants used in the production of BIP polyester resins are recorded in Table 2.1

The acid/anhydrides are charged manually to the reactors as powders with the exception of maleic anhydride which is charged in the molten form. All the glycols are charged directly to the reactor as liquids from stock tanks.

The main reaction taking place during the manufacture of polyester resins is esterification. However, in addition to the main reaction, several side reactions may occur, some of which can reduce the efficiency of esterification. The basic chemistry of the process will be described and the kinetics of the esterification reaction discussed:

Table 2.1 The Main Components used in the Production of BIP Polyester Resins

Reactant	Chemical Structure	Molecular Weight
Maleic Anhydride		98
Phthalic Anhydride		148
Isophthalic Acid		166
Propylene Glycol	 $HO\text{-}\overset{\overset{CH_3}{\vert}}{CH}\text{-}CH_2\text{-}OH$	76
Dipropylene Glycol	 $HO\text{-}CH_2\text{-}\overset{\overset{CH_3}{\vert}}{CH}\text{-}O\text{-}\overset{\overset{CH_3}{\vert}}{CH}\text{-}CH_2\text{-}OH$	134
Ethylene Glycol	$HO\text{-}CH_2\text{-}CH_2\text{-}OH$	62
Diethylene Glycol	$HO\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2CH_2\text{-}OH$	106
* Styrene		104

* Used to blend and cross-link polyesters

2.2 Polyesterification

When an alcohol and carboxylic acid are reacted together an ester is formed:

$$R - COOH + HO - R' \leftrightarrow R - CO - OR' + H_2O$$

Acid + Alcohol Ester + Water.

The reaction is reversible and the water must be removed as it is formed if a good yield of polyester is to be obtained. When the two reactants each contain two reactive groups (eg a dibasic acid and a glycol), an ester can still be formed in the same way:

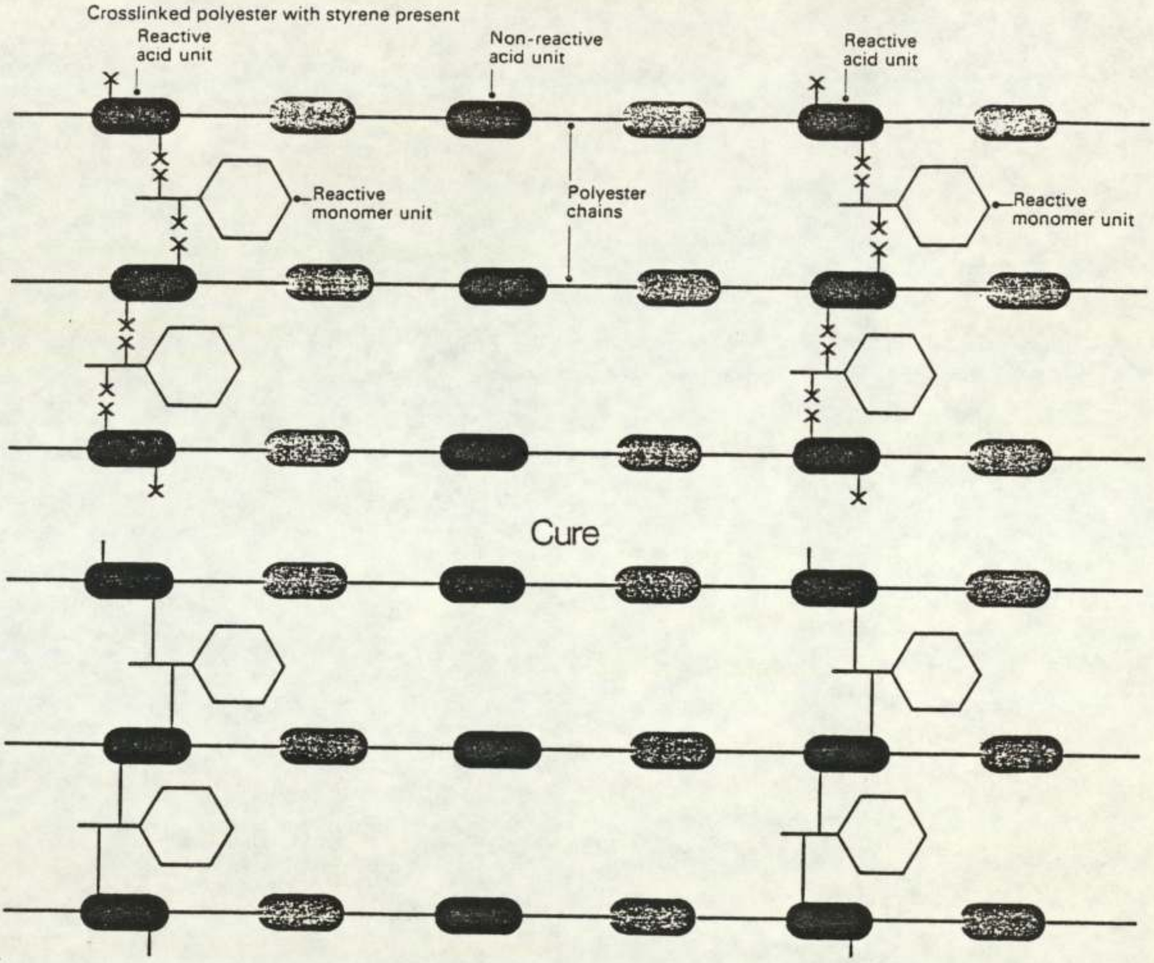
$$HO - OC - R - CO\text{-}OH + HO - R' - OH \leftrightarrow HO - OC - R - CO - O - R' - OH + H_2O$$

This ester has carboxyl and hydroxyl end-groups which can respectively react with more glycol and more acid. In this way, a series of ester units are added together and a polyester is formed:

$$\underbrace{- OC - R - CO}_{\text{Acid}} - \underbrace{O - R' - O}_{\text{Glycol}} - \underbrace{OC - R - CO}_{\text{Acid}} - \underbrace{O - R' - O}_{\text{Glycol}} - \underbrace{OC - R - CO}_{\text{Acid}} - \underbrace{O - R' - O}_{\text{Glycol}}$$

If the dibasic acid is unsaturated (eg maleic anhydride), a reactive polyester is produced[1]. Polyesters produced in this way are solid at room temperature. If, however, a suitable catalyst is added to the molten product, the reactive points (ie across the double bonds of the unsaturated acid) in the polyester chains are caused to link together and a polymer network is formed. The cross links between polyester chain molecules formed in this way are short and frequent, giving a polyester which would be far too brittle for commercial use. Most commercial polyesters are made from a mixture of unreactive and reactive (saturated and unsaturated) dibasic acids. This causes the frequency of cross links to be reduced, allowing variations as required to control resin reactivity. In addition, a third component, usually styrene (see Table 2.1) described as the reactive monomer is included in the "composition". During cure, each of these monomer units is able to combine with two reactive units in adjacent polymer chains, thus forming the crosslinks, which are consequently introduced more readily, and are longer and therefore more flexible. The final crosslinked structure which represents the cured resin system is illustrated as a two-dimensional structure in figure 2.1 (refer to section 2.2.2.1 for the mechanism of cross-linking).

Figure 2.1



Polyester resins are soluble in styrene and so commercial polyesters are therefore produced as solutions of the reactive polyesters in styrene having a high solids content (BIP polyesters are manufactured in the range of 55% to 75% solids) with a moderate viscosity (1.2 to 36 poise) for easy handling.

2.2.1 Determination of the Chemical/Physical Properties of Polyester Resins

The properties of the unsaturated polyester containing the reactive groups can be varied by changing its composition[1]. The reactive acid component is maleic anhydride (during polyesterification most of the maleic anhydride is converted to fumaric acid, see section 2.2.3); different non-reactive (saturated) dibasic acids can be used, but phthalic (ie phthalic anhydride or iso-phthalic acid) is the most common (refer to Table 2.1). The acids are mainly used in the anhydride form, since only half as much water has to be removed in the process. The ratio of saturated to unsaturated acid can be varied and, since different glycols can be used, a wide range of properties can be achieved in the final cured resin (refer to figure 2.1).

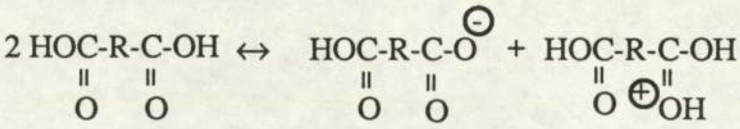
eg 1: In longer chain glycols, the hydroxyl groups are pushed further apart, thus reducing the number of cross links per unit length and giving polyesters with an increased flexibility.

eg 2: Saturated dibasic acids are used to modify the properties of a polyester by pushing the crosslinks further apart, so as to reduce the brittleness of the cured resin. When phthalic anhydride is replaced in a polyester by an equivalent quantity of isophthalic acid, the subsequently crosslinked polyester shows improved flexural modulus, higher heat distortion temperature and better resistance to water and corrosive solutions.

2.2.2 The Mechanism of Polyesterification

The formation of polyesters is via an acid catalysed esterification process. In the absence of an added acid catalyst, a second molecule of reactant acid will serve to catalyse the reaction. An excess of one of the reactants will promote the reaction, as will the removal of one of the products, eg water. The mechanism (reference 2.3) of the polyesterification process takes the following route:

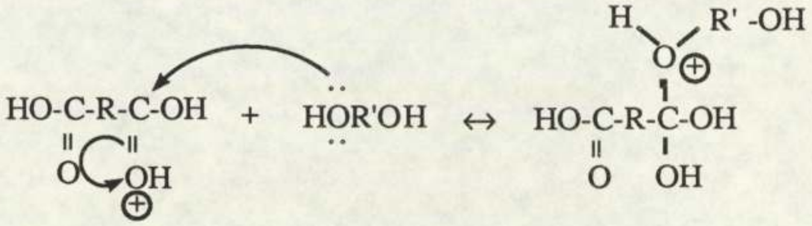
(1)



$$2\,\mathrm{HO\underset{\underset{O}{\|}}{C}\text{-}R\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH} \leftrightarrow \mathrm{HO\underset{\underset{O}{\|}}{C}\text{-}R\text{-}\underset{\underset{O}{\|}}{C}\text{-}O^{\ominus}} + \mathrm{HO\underset{\underset{O}{\|}}{C}\text{-}R\text{-}\underset{\underset{{}^{\oplus}OH}{\|}}{C}\text{-}OH}$$

The carboxylic acid is protonated to produce a species more reactive to nucleophilic attack, ie the second molecule of acid catalyses the reaction.

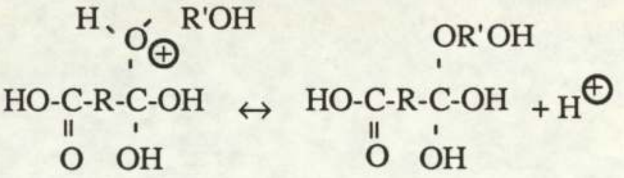
(2)



$$HO\text{-}\underset{\underset{O}{\|}}{C}\text{-}R\text{-}\underset{\underset{\overset{\oplus}{O}H}{\|}}{C}\text{-}OH + HOR'OH \leftrightarrow HO\text{-}\underset{\underset{O}{\|}}{C}\text{-}R\text{-}\overset{\overset{H\diagdown\overset{\oplus}{O}\diagup R'\text{-}OH}{|}}{\underset{\underset{OH}{|}}{C}}\text{-}OH$$

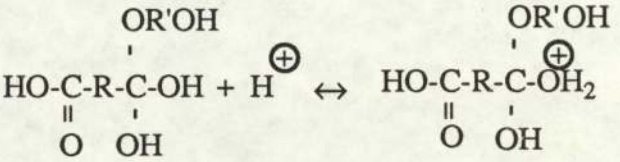
The protonated carboxylic acid then undergoes nucleophilic attack by the glycol. In this stage, as in other additions to a carbonyl group, the carbonyl carbon changes its configuration from trigonal (sp^2 hybridization, 120° bond angles) to tetrahedral (sp^3 hybridization, 109° bond angles), since the number of groups attached to this carbon has increased from three to four.

(3)



$$HO\text{-}\underset{\underset{O}{\|}}{C}\text{-}R\text{-}\overset{\overset{H\diagdown\overset{\oplus}{O}\diagup R'OH}{|}}{\underset{\underset{OH}{|}}{C}}\text{-}OH \leftrightarrow HO\text{-}\underset{\underset{O}{\|}}{C}\text{-}R\text{-}\overset{\overset{OR'OH}{|}}{\underset{\underset{OH}{|}}{C}}\text{-}OH + H^{\oplus}$$

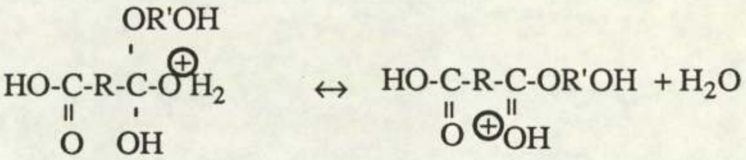
(4)



$$HO\text{-}\underset{\underset{O}{\|}}{C}\text{-}R\text{-}\overset{\overset{OR'OH}{|}}{\underset{\underset{OH}{|}}{C}}\text{-}OH + H^{\oplus} \leftrightarrow HO\text{-}\underset{\underset{O}{\|}}{C}\text{-}R\text{-}\overset{\overset{OR'OH}{|}}{\underset{\underset{OH}{|}}{C}}\text{-}\overset{\oplus}{O}H_2$$

In steps 3 and 4 the shift of a proton produces $OH^{\oplus}_2$ which is a better leaving group than OH.

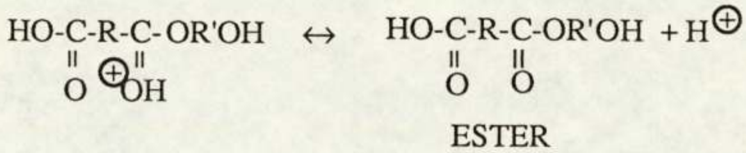
(5)



$$HO\text{-}\underset{\underset{O}{\|}}{C}\text{-}R\text{-}\overset{\overset{OR'OH}{|}}{\underset{\underset{OH}{|}}{C}}\text{-}\overset{\oplus}{O}H_2 \leftrightarrow HO\text{-}\underset{\underset{O}{\|}}{C}\text{-}R\text{-}\underset{\underset{\oplus OH}{\|}}{C}\text{-}OR'OH + H_2O$$

The loss of the $^{\oplus}OH_2$ group yields a water molecule, which must be removed to promote the reaction.

(6)

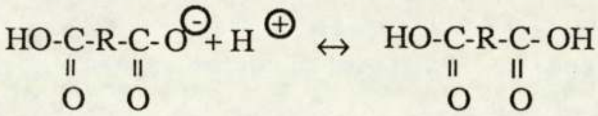


$$\mathrm{HO{-}\underset{\underset{O}{\|}}{C}{-}R{-}\underset{\underset{\oplus OH}{\|}}{C}{-}OR'OH} \leftrightarrow \mathrm{HO{-}\underset{\underset{O}{\|}}{C}{-}R{-}\underset{\underset{O}{\|}}{C}{-}OR'OH} + \mathrm{H}^{\oplus}$$

ESTER

The ester is formed and the acid catalyst regenerated, ie from step (1).

(7)



$$\mathrm{HO{-}\underset{\underset{O}{\|}}{C}{-}R{-}\underset{\underset{O}{\|}}{C}{-}O^{\ominus}} + \mathrm{H}^{\oplus} \leftrightarrow \mathrm{HO{-}\underset{\underset{O}{\|}}{C}{-}R{-}\underset{\underset{O}{\|}}{C}{-}OH}$$

The second carboxylic acid molecule (ie the catalyst) is regenerated.

The ester formed has a carboxyl and hydroxyl functional group at either end, both of which are capable of further reaction to build up longer chains and form a polyester.

2.2.2.1 The Mechanism of Cross-Linking

Polyesters are obtain commercially as solutions of the polyester resin in styrene. These resins require the addition of an accelerator (if unaccelerated) and a catalyst to promote the cross-linking reaction. The customer will mix in the accelerator and catalyst in pre-determined amounts, depending upon gel time (refer to section 4.5), to permit the application of resin to mould surfaces.

2.2.2.1.1 Production of Free Radicals (Initiation)

Cobalt naphthenate (initiator) is mixed with Methyl Ethyl Ketone Peroxide (MEKP - catalyst) to produce free radicals.

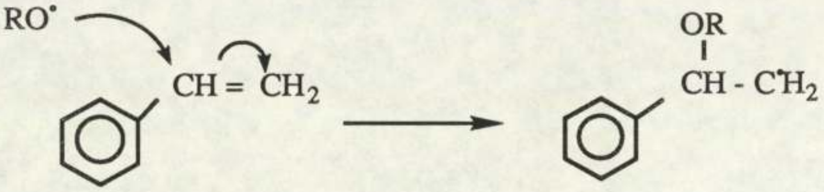
$$\mathrm{Co^{3+}} + \underset{\text{Peroxide}}{\mathrm{ROOH}} \leftrightarrow \mathrm{Co^{3+}} + \mathrm{RO^{\bullet}} + \mathrm{OH^{\ominus}}$$

$$\mathrm{Co^{3+}} + \mathrm{ROOH} \leftrightarrow \mathrm{Co^{2+}} + \mathrm{ROO^{\bullet}} + \mathrm{H^{\oplus}}$$

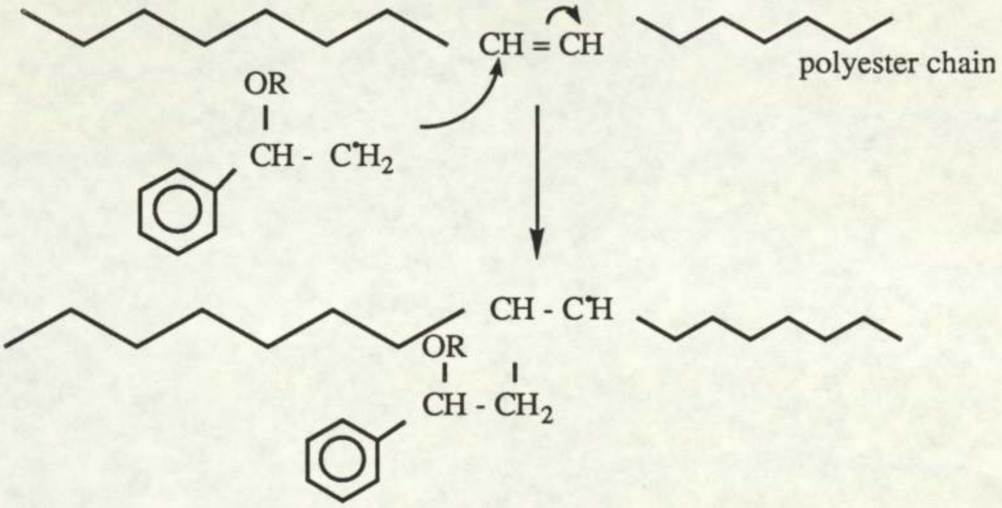
The cobalt may occupy two oxidation states in the reacting mixture, thus producing two types of free radical ($RO^{\bullet}$, $ROO^{\bullet}$). These free radicals may now interact with the styrene to promote cross-linking.

2.2.2.1.2 Propagation of Cross-Linking

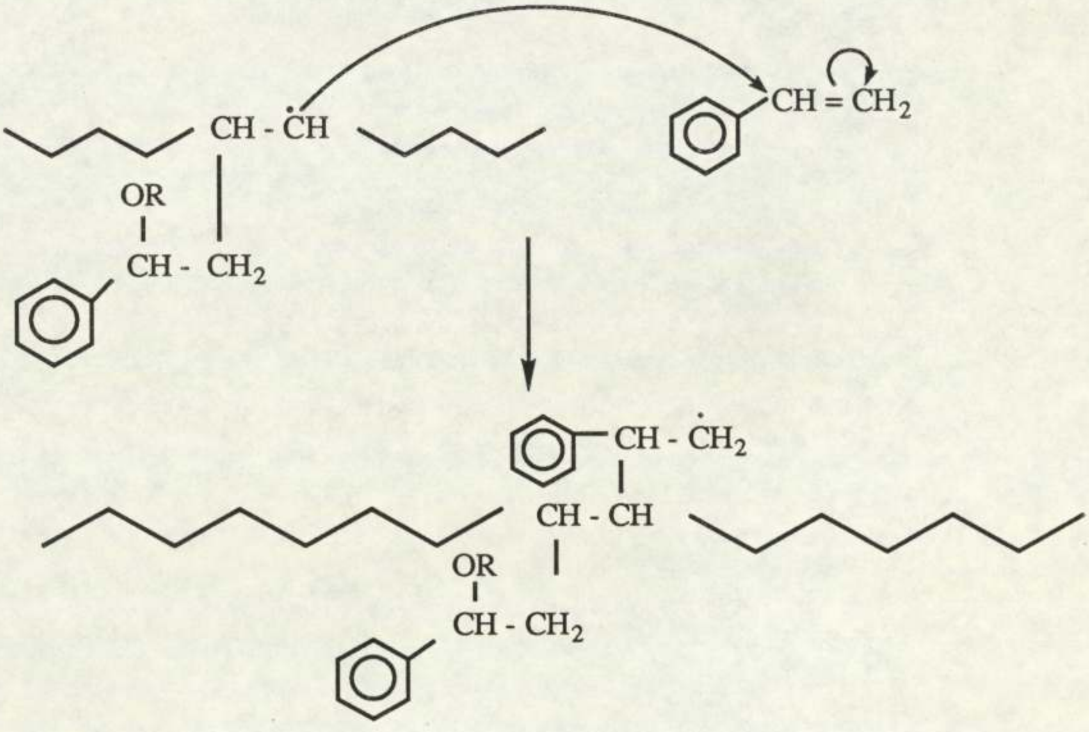
The free radicals produced react with the styrene monomer to yield another free radical capable of forming links across the double bonds of the polyester chains.



The styrene free radical now attacks the electron rich double bonds in the polyester chains, ie those belonging to the maleic anhydride.



The double bond is broken and another free radical is formed which will react with another styrene molecule.

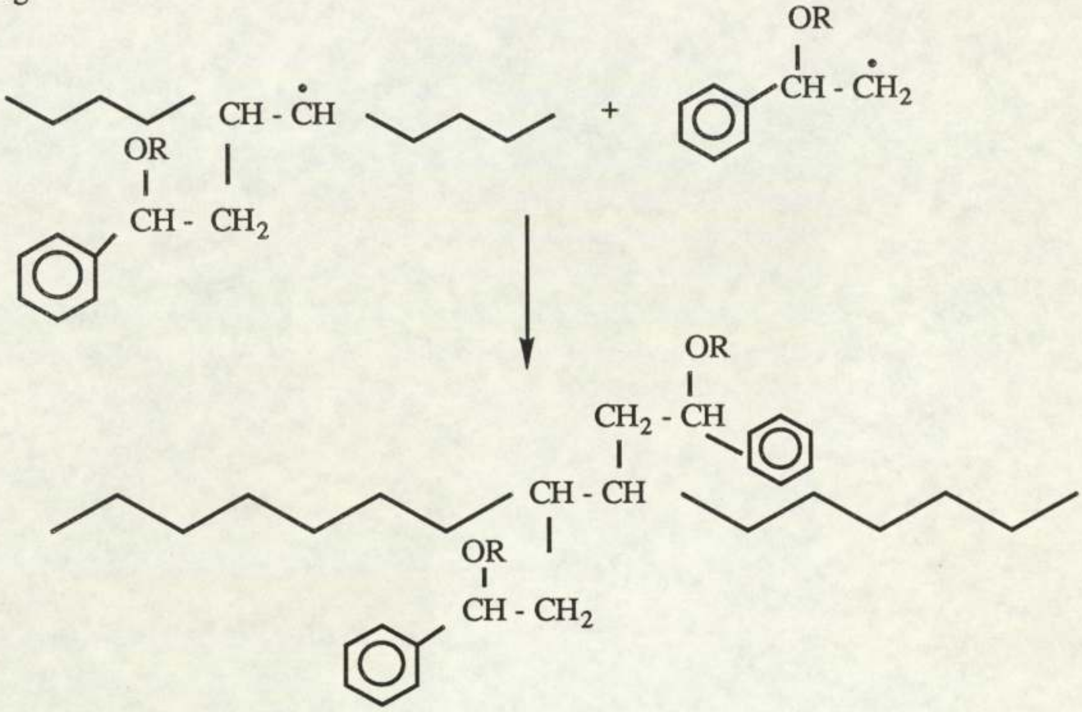


The process is repeated and a structure similar to the one illustrated in figure 2.1 is developed.

2.2.2.1.3 Termination of the Free Radical Mechanism

The free radical cross linking mechanism may be terminated by the combination of two free radicals.

eg

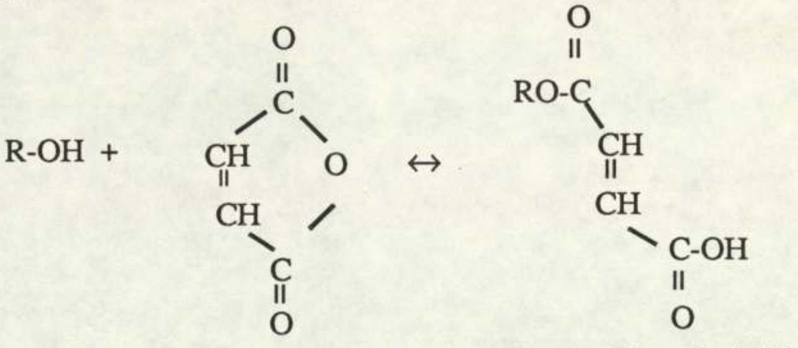


The process may occur at any time and on any chain, thus resulting in a range of cross-linked networks.

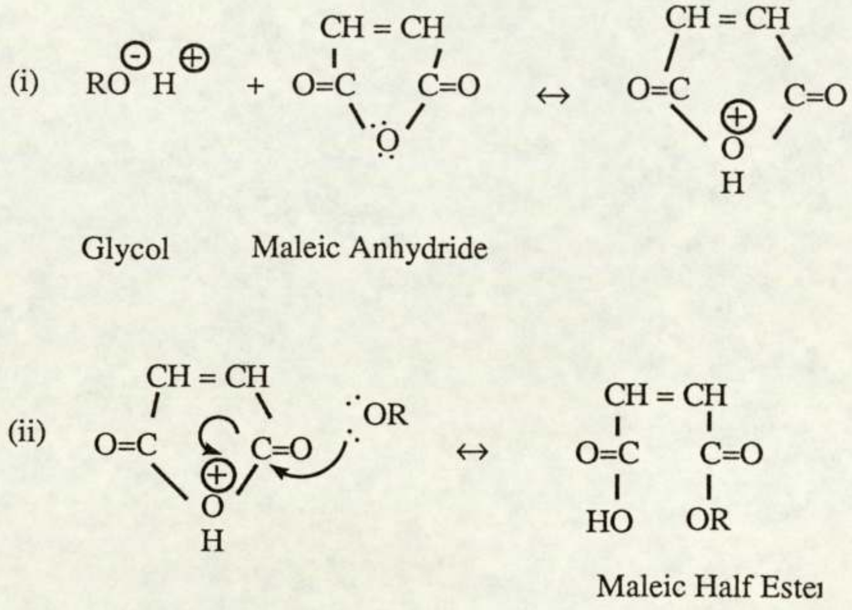
2.2.3 Conversion of Maleic Anhydride to Fumaric Acid

During the preparation of polyesters most of the maleic anhydride is converted into its geometrical isomer, fumaric acid

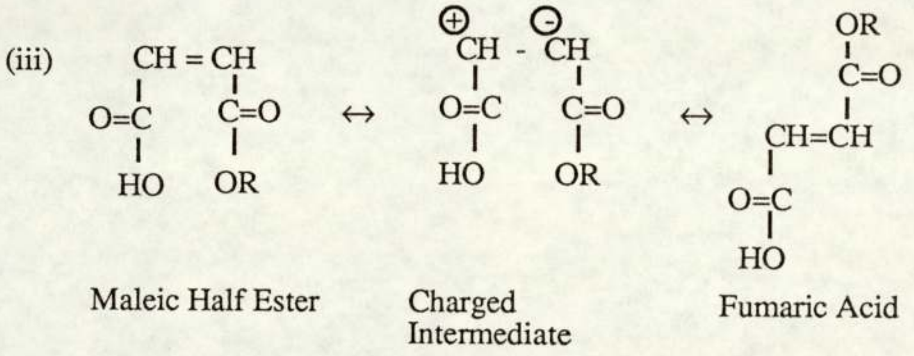
ie



Approximately ninety per cent of the maleic anhydride charge will undergo such a transformation. The mechanism for the isomerisation[4] is as follows:-



In steps (i) and (ii) the attack of the glycol opens the ring of the maleic anhydride to yield the maleic half ester (*cis* configuration).



The maleic half ester (*cis* configuration) isomerises via a dipole mechanism[4] to yield fumaric acid (trans configuration).

Since no isomerisation could take place around the double bond of the maleic anhydride (due to the fact that the double bonds are very rigid and cannot rotate) a dipole is thought to exist[4] which subsequently isomerises to the trans fumaric product.

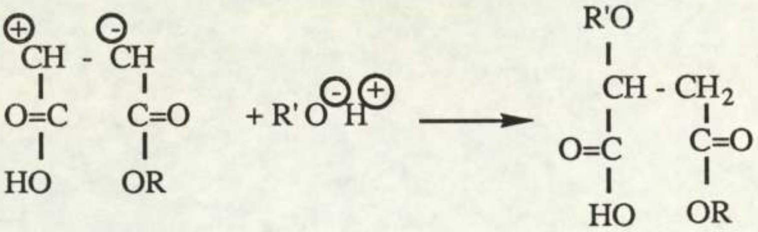
NB - Stage 3 is only a proposed mechanism for the conversion of the *cis* maleic half ester to the trans fumaric acid.

2.2.4 Side Reactions

During the polyesterification reaction, side reactions may occur which can reduce the efficiency of the process.

2.2.4.1 Branching

As mentioned in section 2.2.3, approximately ninety per cent of the double bonds belonging to maleic anhydride undergo *cis* to trans isomerisation, resulting in the formation of fumaric acid. However, some of the double bonds react in the early stages of the polyesterification process with excess glycol to yield addition products and hence branched chains.

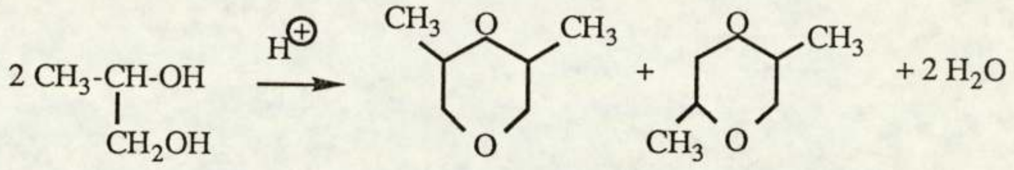


If the charged intermediate exists (refer to stage (iii) in section 2.2.3), then some of the double bonds may be lost due to the addition of glycol across them. Approximately 10% of the double bonds are lost in this way. In an ideal system (ie one in which no branching exists) it should be possible to process to an infinite chain length. However, if braching exists, then after processing to a certain acid value (see chapter 4) crosslinking may occur, which will result in gelation of the resin.

2.2.4.2 Conversion of Glycols to Volatile Derivatives

In the presence of acid, propylene glycol (the most widely used glycol in the synthesis of BIP unsaturated polyesters) may decompose to produce a mixture of cyclic ethers[4].

eg



2,6 - dimethyl- 1,4 - dioxane

2,5 - dimethyl - 1,4 - dioxane

Both derivatives are volatile and may be lost from the reaction mixture.

2.3 The Kinetics of Polyesterification

The kinetics of the polyesterification reaction are complex[5]. Initially the medium is an equimolar mixture of alcohol and acid, whereas at complete reaction it is an ester. Normally, such a large change in polarity would not be acceptable in kinetic studies. The initial mixture is also very concentrated and it is likely to be thermodynamically non-ideal in the sense that the activities of the two reactants may not be proportional to their concentrations. This leads to two possible conclusions:

(1) It is only meaningful to consider the later stages of the reaction, eg when more than 80% of the functional groups have reacted.

(2) Kinetic analysis over the whole course of the reaction is of value.

Depending on which conclusion is reached, a different kinetic order can be deduced from a given set of results.

2.3.1 The later stages of the reaction (ie >80% functional groups have reacted)

As the reaction proceeds the effect of molecular weight and viscosity of the medium become greater influences on the reaction rates.

Esterification of an alcohol and an acid is an equilibrium reaction.

$$\text{acid} + \text{alcohol} \leftrightarrow \text{ester} + \text{water} \qquad (2.1)$$

If the water of reaction is removed as soon as it is formed, the reverse reaction of ester hydrolysis can be eliminated:

$$\text{acid} + \text{alcohol} \rightarrow \text{ester} + \text{water} \uparrow \qquad (2.2)$$

The course of the reaction (or rate of reaction) can be followed by measuring the rate of loss of carboxyl groups (or acid value, see chapter 4).

It has been suggested[5] that the rate of the polyesterification process without added catalyst should be written:

$$\frac{-d\,[COOH]}{dt} = K\,[COOH]^{2}\,[OH] \qquad (2.3)$$

(the minus sign indicates the removal of carboxyl groups)

ie the rate is second order with respect to the acid and first order with respect to the glycol; therefore the rate is overall third order.

If the carboxyl and hydroxyl group concentrations are equal and of concentration c, then equation (2.3) becomes:

$$\frac{-d[COOH]}{dt} = Kc^{3} \qquad (2.4)$$

$$\rightarrow \frac{-dc}{dt} = Kc^{3}$$

$$\rightarrow \int \frac{dc}{c^{3}} = \int -Kdt$$

$$\frac{C^{-2}}{-2} = Kt + \text{constant}$$

$$\text{Therefore, } 2\,Kt = \frac{1}{C^{2}} - \text{constant} \qquad (2.5)$$

A factor p (extent of reaction) is introduced and represents the fraction of functional groups (carboxyl) initially present that have undergone reactions in a given time t. Then $c = (1 - p)C_o$, where C_o is the initial concentration of functional groups. Hence, equation (2.5) becomes:

$$2\,C_o\,Kt = \frac{1}{(1 - p)^2} - \text{constant} \tag{2.6}$$

There is some concern over the accuracy of these rate studies:

In the absence of an added catalyst, an esterification reaction is slow, and to attain an acceptable rate of reaction it is necessary to use high temperatures. Also to study the kinetics satisfactorily, it is desirable to avoid the reverse reaction of hydrolysis by removing the water that is formed. The removal of this water may involve the loss of some of the volatile components (eg glycol), thus introducing further error into the calculations.

The conclusion from results quoted in the literature[5] show <u>the reaction to be overall third order; second order in carboxyl and first order in hydroxyl</u>.

The mechanism is thought to follow the route suggested in seciton 2.2.2, where the Rate Determining Step is stage 2.

2.3.2 The Whole of the Reaction

Other workers (5) have quoted a two and a half order relationship for 0 - 93% of the reaction.

Some have interpreted the reaction in terms of second order kinetics and others a change in the kinetic order from second order initially to third order in the later stages.

The disagreement over which kinetics give the best fit probably results from the failure to distinguish clearly between the time interval over which results give a straight line when plotted for a given kinetic order and the amount of reaction which has taken place in this time. For example, some typical results are:

A third order plot for 12.7% (80% to 92.7%) of the reaction but for 45% of the time of the reaction, and a second order plot for 35% of the reaction and 15% of the time.

ie kinetic studies over the whole of the reaction may be misleading due to the fact that most of the reaction occurs in a short time.

Further confusion is encountered in attempting to assign a kinetic order to the whole reaction when the order of reaction in acid and hydroxyl groups is examined for the claimed two-an-a-half order reactions, ie

$$\frac{-d\,[COOH]}{dt} = K\,[COOH]^{1.5}\,[OH]$$

In the preceding discussion on the kinetic order of the polyesterification reaction, it was assumed that the reactivity of the functional groups did not depend on the size of the molecule to which they were attached.

However, in many polymer systems the functional groups are in an environment which affects their reactivity. Hence, molecular size and complexity do have an influence on reactivity. Care is therefore needed when applying the concept of equal reactivity of functional groups, as not all systems meet the requirements.

2.4 References

1 How Polyester Resins are Made, BIP Technical Sales Literature.

2 Introduction to Organic Chemistry, 3rd Edition, A Streitweiser, C H Heathcock, 465-6

3 Principles of Organic Chemistry, 2nd Edition, J Kice, E N Marvel, 379-381, 1974.

4 Examination of Source Factors Affecting the Molecular Size Distribution of Unsaturated Polyester Resins and their Influence on Moulding Performance in DMC; BIP Technical Report 120, B Y Downing, A D Brain.

5 Polyesterification, 3-21, D H Solomon, Division of Applied Chemistry CSIRO Melbourne, Australia, 1972.

CHAPTER 3

COMMERCIAL PRODUCTION

3 COMMERCIAL PRODUCTION

3.1 General Manufacturing Procedure

The production of polyester resins can be divided into four distinct stages. These stages occupy a total processing time of approximately thirty hours. Three production processes are used, each of which will incorporate the four manufacturing stages. Resin type will determine which product process is selected.

A description of each stage and the product processes follows:

(Figure 3.1 shows a simplified flow diagram for a BIP polyester resin product process.)

3.1.1 Charging

The glycol(s) are volumetrically charged to the reactor and the agitator started. The acid is then charged manually, from bags to the reactor and heat up started. (Note: Maleic anhydride may also be charged in a molten state.)

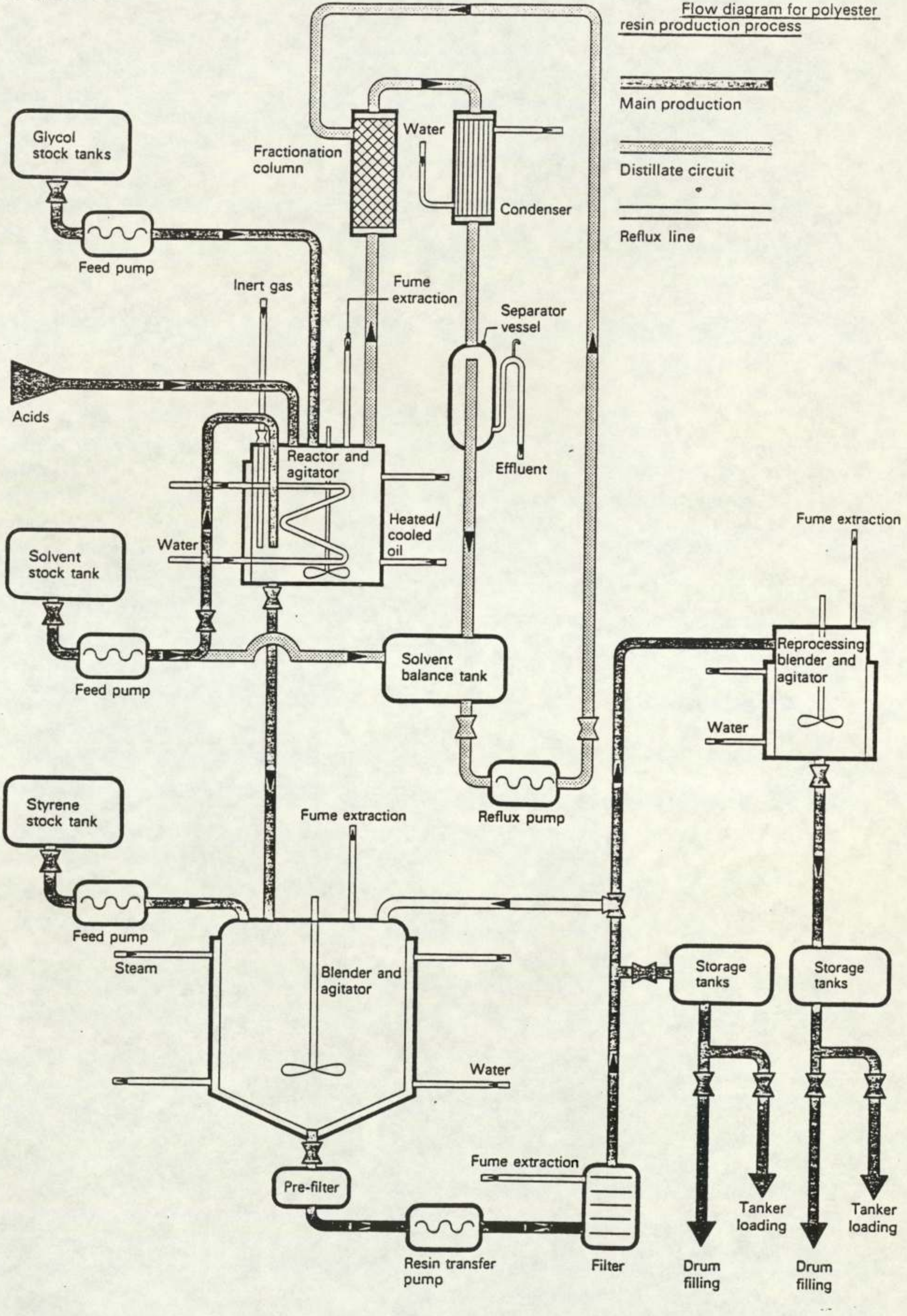
Refer to Table 2.1 for the main reactants used in the production of BIP polyesters.

3.1.2 Reaction

The acids and glycols are reacted together at a temperature of about 215°C. When top temperature is reached, ie 215°C, the reacting resin is tested every hour for both viscosity and acid value. The acid value is controlled within certain limits by the addition of either glycol (high acid value) or acid (low acid value). When the reaction is complete as shown by acid number and viscosity, cooling is applied and the reaction stopped (refer to Chapter 4 for in-process testing).

The reaction times are dependent on charge type, but are in the region of 20-40 hours. Water is formed as the by-product of the esterification reaction and must be removed to promote the reaction (refer to Chapter 2 - Process Chemistry). Reflux distillation columns and condensers are used to control water removal, but retain the other volatiles (eg glycols) in the charge. To

Figure 3.1



Flow diagram for polyester resin production process prevent discolouration and pre-gellation, oxygen must be excluded and the reaction is carried out in an inert atmosphere.

3.1.2.1 Two-Stage Reactions

Most resin production follows the procedure discussed in section 3.1.2. However, some resins require a second stage to process. These are the resins that contain isophthalic acid:

Isophthalic acid is a low reactive species and if included in a one-stage process with maleic anhydride, will compete for reaction with the glycol. The more reactive maleic anhydride will win the competition for reaction with the glycol leaving the majority of the isophthalic acid unreacted. This will not yield the desired product and so a two-stage process is used. The first stage of reaction enables the less reactive isophthalic acid to react with the glycol, while the second stage is the reaction of this material with the more reactive maleic anhydride. Both stages of reaction will follow a procedure similar to the one discussed in section 3.1.2.

3.1.3 Blending

When the reaction is complete, the molten product is cooled to approximately 150°C and transferred from the reactor to the blender containing the monomer (styrene). Inhibitors (usually hydroquinone) are added at this stage to improve stability. The resin is blended to the desired solids content by mixing the correct ratio of resin:styrene. Polyester resins are usually supplied commercially as styrene solutions of this type. If the properties (refer to Chapter 4) are in balance, the resin is either reprocessed (see next section) or run off.

3.1.4 Packaging or Reprocessing

After blending, the resin may be suitable for customer use, in which case the batch is transferred to a holding tank ready to be drummed off or loaded onto a tanker.

However, many resins require the incorporation of various additives to provide the desired properties. In this case, the resin is transferred to another blender and mixed with the appropriate additives. Resins used in this way are referred to as **base resins**, while the final product is known as a **reprocessed resin**. When complete, the reprocessed resins are drummed off for distribution to the customer.

3.2. Production Process

Three processing methods are available for the manufacture of polyester resins each concerned with the removal of water from the reactor. The processes involved use different overhead equipment and the method selected will depend on the type of resin being manufactured.

3.2.1 Fusion Process

Originally, vapours evolved during the reaction were passed through a packed column. Column top temperature was not controlled since there was no reflux taking place. A consequence of this procedure was high glycol losses and so the fusion process was only used for part of the reaction and then followed by one of the other processes.

The glycol losses (due to a large price increase) prompted the need for better control of this process. Successful work by the Teaching Company Scheme[6] has led to the use of improved partial condensers for the fusion process.

The vapours (glycol and water) are passed through a packed column where separation occurs, ie glycol is returned to the reactor and water removed. The column top temperature is maintained at about 105°C by controlling the reactor heat up rate and the cooling water flow rates to the condenser on top of the packed section. Glycol losses have been significantly reduced and the fusion process is being sought to replace both the distillate reflux (refer to section 3.2.2) and solvent processes (refer to section 3.2.3).

3.2.2 Distillate Reflux

The vapours evolved from the reaction are passed through a packed column where separation of the glycol and water takes place. However, a proportion of the distillate from the total condenser is fed back to the top of the packed column to control the column top temperature. This results in water being returned to the reactor, thus increasing reaction times for resins manufactured by this process. In addition to extended reaction times, glycol losses are significant. It is the intention of BIP to replace the distillate reflux process with the fusion process (refer to section 3.2.1), thus reducing reaction times and glycol losses for resins currently manufactured via this process.

3.2.3 Solvent Process

This method relies on an azeotropic agent to aid the removal of water from the reactor system:

Xylol is added to the reactants to form a low boiling point azeotrope with water. The azeotropic mixture is then passed through a packed column and a condenser to a separator (refer to figure 3.1). The two immiscible components are separated and the xylol transferred to a balance tank for re-use while the water is discharged into the effluent line.

This procedure gives good separation of water and glycol, but it is necessary to increase the heat input at the end of a batch to remove the xylol. The solvent process cannot be effectively used for all resins, since the xylol lines suffer blockages. As mentioned earlier, it is hoped that the fusion process will replace the solvent and distillate reflux processes. This will hopefully eliminate the problems encountered when manufacturing resins via these procedures, and also allow the adoption of a standard manufacturing process

(Note: Some two-stage reactions may involve a combination of two processes:

eg	stage one	-	fusion
	stage two	-	solvent.

Most will use the same procedure in stage two as in stage one.)

3.3. Production Equipment

The production facility under investigation by the Teaching Company Scheme consisted of a number of stainless steel reactors, fitted with heating/cooling jackets/coils and having different capacities. Variations exist in the overhead equipment: some reactors have partial condensers in addition to a packed column, while others operate using only a packed column. Figure 3.1 provides a simplified flow diagram for a typical BIP polyester resin production process.

The main feature omitted from this diagram is the partial condenser which sits on top of the reactor and is connected to the condenser/separator line.

In addition to the reactor and overhead equipment, the flow diagram also shows the blending and reprocessing systems associated with the production of BIP polyester resins.

Reference 6 - Private Communication, Jane Sims, BIP Chemicals

CHAPTER 4

PROCESS CONTROL AND PRODUCT TESTING

4 PROCESS CONTROL AND PRODUCT TESTING

4.1 Introduction

During the processing of polyester resins, two control tests are performed, namely acid value and PRS viscosity (see page 45). The results of these tests are plotted against each other to monitor the progress of the reaction (refer to figure 4.1). Testing begins after reaching reactor top temperature, ie approximately 200°C, and every hour until the required specification is obtained. When complete, the resin is blended to the specified solids content and a sample sent to the Quality Control Laboratory for information only (FIO), ie to determine viscosity, solids and gel time. Depending on the FIO results the resin is either adjusted or approved for a Final sample. The quality control tests used when passed for finals are: acid value, cone and plate viscosity, solids, gel time and stability.

Some resins are blends of a base resin with various additives. In this case, product testing will be limited to the quality control tests mentioned above. However, if the product contains an inorganic additive, an ash test will be required in addition to the above tests. There is a set procedure used for each of these tests which is described in the following sections, since some of them provide a significant contribution to the work of the project:

ie as a result of this research project, alternative quality control tests have been developed for both solids and ash (refer to Chapter 5).

4.2 Acid Value

Acid value provides an indication as to the number of carboxyl groups that remain unreacted in the resin solution. Each resin requires processing to a specific acid value. The acid value range is typically 10 - 35 mgKOH/g for polyester resins and is measured by titration: 1 g of resin is accurately weighed into a 250 ml conical flask and dissolved in 25 ml of acetone. Two to three drops of Phenolphthalein Indicator solution are added and the solution titrated with standardised Alcoholic Potassium Hydroxide solution (O.1N).

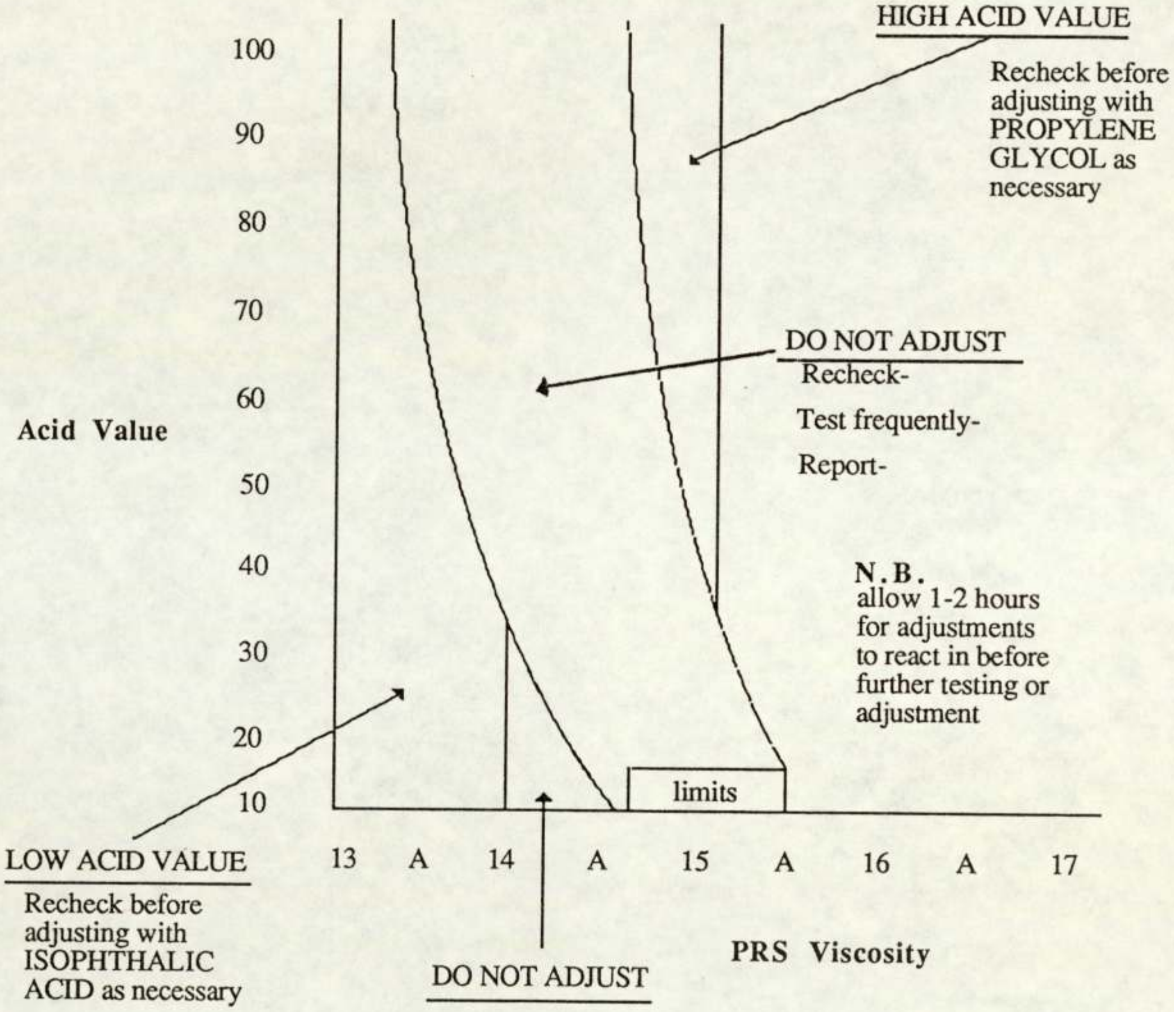


Figure 4.1; Acid Value Vs Viscosity

The acid value is calculated for either the solid resin, the blended resin or both, depending upon resin type.

4.2.1 Acid Value Calculation

(a) Solid Resin - mgKOH/g

$$\text{Acid Value} = \frac{V \times F \times 100}{W \times Y} \tag{4.1}$$

(b) Blended Resin - mgKOH/g

$$\text{Acid Value} = \frac{V \times F}{W} \tag{4.2}$$

where

V = Sample Titration (ml)
W = Weight of Sample Taken (g)
F = Factor of O.1N Alcoholic Potassium Hydroxide
Y = Solid Resin Yield of the Liquid Resin

Acid value is expressed in terms of mg of Potassium Hydroxide required to neutralise each gram of resin.

4.3 Viscosity (PRS Tube)

Viscosity is measured every hour during the reaction stage of resin production. Viscosity is determined by comparison with a set of standard Paint Research Station (PRS) bubble tube viscometers:

An empty clean PRS viscosity tube is filled to the mark with the resin solution to be tested. It is then sealed and placed for at least 30 minutes in a water bath containing the standard PRS viscometers at 25°C ± 0.5°C. The viscosity of the resin solution is determined by comparing the rate of bubble travel, after inversion of both the sample and one of the standard tubes. The PRS tubes are numbered and the PRS viscosity of the resin is quoted as the number on the standard tube which has an equivalent rate of bubble travel.

4.4 Viscosity (Ferranti-Shirley Cone and Plate Viscometer)

The viscosity of the blended resin (FIO and Final) is measured to a higher degree of accuracy than the PRS method by use of a cone and plate viscometer.

A sample of resin is sheared at a constant rate between a rotating cone and a stationary plate. The transmitted torque is measured and used to calculate the resin viscosity.

(Note: In some cases the viscosity is measured at two different shear rates and may even be expressed as a ratio of the two (Thixotropic Index).)

Both the cone and the plate are kept at a constant temperature by circulating water through them from a thermostatically controlled water bath. The instrument is calibrated daily in accordance with BS 5750 requirements to yield reliable results.

4.4.1 Test Method

(a) With the plate lowered, sufficient sample is placed on it just to fill the gap between the cone and plate in the closed or operational position. The sample should be placed in the centre of the plate and should be free from foreign bodies and air bubbles.

(b) The cone speed is set to the required value using the speed control dial on the control unit:

eg (i) 3.0 rpm
(ii) 0.1 rpm and 3.0 rpm
(iii) 3.0 rpm and 9.0 rpm.

Different resins will require one of the above three combinations of cone speed.

(c) The scale reading is set to X1.

(d) The plate is carefully raised into the operational position.

(e) The indicator needle is observed and in order to obtain a reading between 20 and 80 divisions, the scale reading sensitivity switch is altered (X1 to X5).

(f) When the scale reading has become steady it is recorded and used to calculate the resin viscosity as shown in section 4.4.2.

(Note: If a second cone speed is required, adjust the speed control dial and repeat (e) and (f).)

(g) The speed control is turned to zero and the indicator needle allowed to fall to zero.

(h) The plate is finally lowered and thoroughly cleaned along with the cone.

4.4.2 Viscosity Calculation

The viscosity of the sample examined at the particular shear rate is calculated from the following expressions:

$$\text{Viscosity (Poise)} = \frac{\text{Sensitivity Setting x Scale Reading x Viscosity Constant}}{\text{Cone Speed (rpm)}} \qquad (4.3)$$

(Viscosity range = 1.2 to 36 poise)

Where

$$\text{Shear rate (sec}^{-1}\text{)} = \text{Cone Speed (rpm) x Shear Rate Constant} \qquad (4.4)$$

$$\text{Thixotropic Index} = \frac{\text{Viscosity at 3.0 rpm}}{\text{Viscosity at 9.0 rpm}} \quad \text{or} \quad \frac{\text{Viscosity at 0.1 rpm}}{\text{Viscosity at 3.0 rpm}} \qquad (4.5)$$

The shear rates used to determine Thixotropic Index will depend on the resin type.

The viscosity and shear rate constants used in the determination of viscosity are shown in Table 4.1.

Table 4.1 Viscosity and Shear Rate Constants for the Ferranti-Shirley Viscometer

Cone	Viscosity Constant	Shear Rate Constant
Large	0.30	18.35
Medium	1.77	17.28
Small	14.30	16.40

All polyester resins are analysed using the large cone.

4.5 Gelation Time

The gel time test, as the name suggests, provides an indication of how long it takes the resin to gel and is particularly useful for the customer when applying resins to mould surfaces. Gel time is dependent on many factors:

eg resin reactivity
inhibitor, catalyst and accelerator content

and the test will encompass each when deducing a time. The gel time range for polyesters is 3 - 150 minutes. Both the FIO and Final samples are tested for this property.

4.5.1 Unaccelerated Resins

- resins where the customer adds both the accelerator and catalyst.

(a) Set up the gelation timer in such a way that the spindle can move vertically in the centre of an empty aluminium container which is partially immersed in a water bath at 25°C.

(b) Weigh 100 g of polyester resin into the aluminium container and allow the sample to equilibrate at 25°C.

(c) Add 2 mls ± 0.05 mls of Methyl Ethyl Ketone Peroxide (MEKP) catalyst and mix into the resin for two minutes.

(d) Add 1 ml ± 0.03 mls of accelerator (eg cobalt naphthenate), previously brought to 25°C, and stir into the mix vigorously for two minutes.

Start the timer at the moment the accelerator is added so that the time taken to mix in the accelerator is recorded as part of the gel time of the resin; re-position reciprocating spindle into the resin sample.

(e) If necessary adjust the spindle of the gelation timer so that the disc is completely immersed in the resin for its full stroke and at its lowest position the disc shall be between 1 cm and 2 cms from the bottom of the container.

(f) The motor will cut out at the onset of gelation of the resin and the counter will give the gel time of the resin in minutes at 25°C.

4.5.2 Pre-Accelerated Resins

- resins whose accelerator is added on the plant.

Follow the above procedure with the exclusion of the addition of the accelerator.

Start the gelation timer immediately before stirring in the MEKP at 25°C.

4.6 Solid Resin Yield

The solids content, as measured by the oven solids test method, is required to be within a certain specification, eg 70% ± 2.0%. Polyesters manufactured by BIP have a solids content within the range 55% to 75%. This is achieved by blending the correct ratio of resin: solvent or resin, additives, fillers: solvent. The traditional oven solids content measured on both FIO and Final samples is to be replaced by Microwave Solids, a new quality control test, see Chapter 5. There are many variations of the oven solids test used in industry and the results will vary depending on the particular test adopted. The method for polyester resins has used a conventional oven at 150°C:

A clean tin plate dish, 7 cm in diameter and 1 cm deep, is dried for at least 30 minutes in an oven at 150°C and after cooling in a desiccator, is weighed to the nearest milligram (W1). 2.0 g ± 0.2 g of the resin sample are weighed into the dish and the sample weight recorded to the nearest milligram (W2). The contents of the dish are spread as evenly as possible over the bottom of the dish by tilting. The dish and contents are then placed on a perforated sheet metal shelf and put into an oven which is maintained at a temperature of 150°C ± 2°C throughout the determination. After one hour, the dish is removed from the oven, allowed to cool in a desiccator and reweighed (W3). The test result is then calculated from equation 4.6:

$$\text{Solid Resin Yield (SRY)} = \frac{W3 - W1}{W2} \times 100\% \tag{4.6}$$

The test is performed in duplicate and the result reported as the mean of the two determinations provided the two determinations do not differ by more than one unit, ie 1.0%.

For routine determinations on polyester resins it is not necessary to use a desiccator provided the weighings are carried out within half an hour of removing the samples from the oven. However, in the event of a dispute, a desiccator must be used.

Ash content is performed on the FIO and Final samples of resins that contain inorganic fillers/pigments. The ash content is required to be within a certain specification range, eg 13.0% to 14.3%. However, polyester resins are manufactured over the range of 2.0% to 29.5% ash content, depending on filler content. The traditional oven ash procedure has now been replaced by a Microwave Ash test, see Chapter 5. Several variations of the oven ash test exist and the chosen test will depend upon the type of inorganic material present in the resin. However, polyester resins are analysed using a standard method:

A clean silica crucible and lid are placed on a muffle furnace at 800°C for 15 minutes and cooled in a desiccator for approximately 45 minutes. The crucible and lid are accurately weighed to the nearest milligram. 5 g ± 0.2 g of the resin sample are weighed into the crucible and the sample weight recorded to the nearest milligram (S). The crucible and lid are placed on a pipeclay triangle over a low bunsen flame and the heat slowly increased so as to complete any initial decomposition or to cause the material to ignite and burn away. The crucible is then placed in the muffle furnace at 800°C and the lid tilted slightly to allow free access of air. The crucible is removed from the muffle after one hour and placed in the desiccator to cool. The crucible and contents are allowed to cool for approximately 45 minutes and then reweighed, to obtain the weight of residue (R). The ash content is then calculated from equation 4.7:

$$\%\,\text{Ash} = \frac{100 \text{ x R}}{\text{S}} \tag{4.7}$$

4.8 Stability

The stability of resins is monitored to provide an indication of the shelf life of the product.

Two 4 oz bottles are filled to approximately two-thirds their depth and sealed. One of the bottles is then placed in a 55°C oven and examined daily until gelation occurs or until five days have elapsed, whichever is the sooner. The second bottle is placed in the 100°F chamber and examined twice weekly until gelation occurs.

If the resin does not gel within five days in the 55°C oven, it is expected that the resin will have an acceptable shelf life.

CHAPTER 5

MICROWAVE SOLIDS AND ASH

5 MICROWAVE SOLIDS AND ASH

5.1 Introduction

As part of the FIO and Final quality control testing of polyester resins an oven solids test is performed (see section 4). Solids content analysis, therefore, is a very important measurement and needs to be tested accurately.

There are, however, problems associated with the oven solids test. Firstly, the test itself has been shown to have a very poor reproducibility. The accuracy of this test method is shown in this work to be about ± 1.0% which in a ± 2.0% product specification is totally unacceptable. Secondly, the test is time consuming, taking about one-and-a-half hours, so it is unsuitable for on-line testing; this may cause hold-ups in the production plant whilst resins wait for clearance before being transferred to storage.

The above weaknesses highlighted the need for an alternative technique that will be more accurate/reproducible and quicker than the present oven method.

Previous work[7] evaluated ultrasonic and infrared solids testing equipment and density as alternative test methods without any success.

The present work shows how microwave equipment can be used to measure the solids content of polyester resins both more quickly and to a higher degree of accuracy than is presently achievable.

In addition to solids content, the same instrument is capable of determining ash content. The present oven ash method (see section 4) is also very time consuming (taking about 2.5 hours) and therefore unsuitable for on-line testing, since hold-ups may be encountered for resins awaiting clearance from this test.

The microwave system was, therefore, evaluated for both test methods and for this reason the chapter will be divided into two main subsections; Solids and Ash.

5.2 Theory

5.2.1 Introduction to Microwave Principles

Microwaves are a form of electromagnetic energy. This form of energy has alternating electric and magnetic fields which travel at the velocity of light. Microwave energy is below the visible light and infrared regions of the electromagnetic spectrum and above radio waves.

If a material absorbs microwave energy, it will increase in temperature. However, microwaves are not a form of heat which must be conducted from one material to another. Conventional heating requires conduction of thermal energy through solids, liquids and gases to raise the temperature of a material. Conduction of heat is a slow process. Any material can be heated by conduction but only certain materials can be heated by microwaves, ie only if microwaves are absorbed.

5.2.1.1 Mechanisms of Microwave Absorption by Liquids

5.2.1.1.1 Dipole Rotation

Permanent or induced electric dipoles in absorbing molecules will rotate in response to the applied microwave electric field. (see Figure 5.1) The electric dipole of the molecule rotates as it attempts to align with the oscillating electric field of the microwave. This causes the entire molecule to rotate, first in one direction and then in the opposite direction, causing it to collide with neighbouring molecules. Because of the microwave frequency these collisions occur several billion times a second and quickly raise the liquid temperature. It is thought a dipole exists across the carbon-carbon double bond of styrene, allowing the above process to occur, resulting in the evaporation of styrene molecules from blended polyester resins.

5.2.1.1.2 Ionic Conduction

Liquids containing dissolved ions can conduct current. Ions in the liquid can migrate in the presence of the microwave electric field. (see Figure 5.1) The ions move first in one direction and then in the opposite, since the microwave electric field reverses sign several billion times each second. As the ions move, they collide with other molecules in the liquid, resulting in an increased temperature and, subsequently, evaporation of any volatiles present.

5.2.1.2 Mechanism of Microwave Absorption by Solids

If the microwave electric field can penetrate a solid material it can sometimes cause electrons in the material to migrate due to its presence. This electron migration is resisted by charge distribution around each molecule or atom in the absorbing solid.

The movement of electrons in response to the microwave field causes generation of heat similar to that produced in a simple electric circuit by resistance.

5.2.2 Drying Techniques

5.2.2.1 Limitations on Drying Speed

(i) Convection (Oven) Drying:- Rate limiting step is conductance of heat from the heating source through air to the sample.

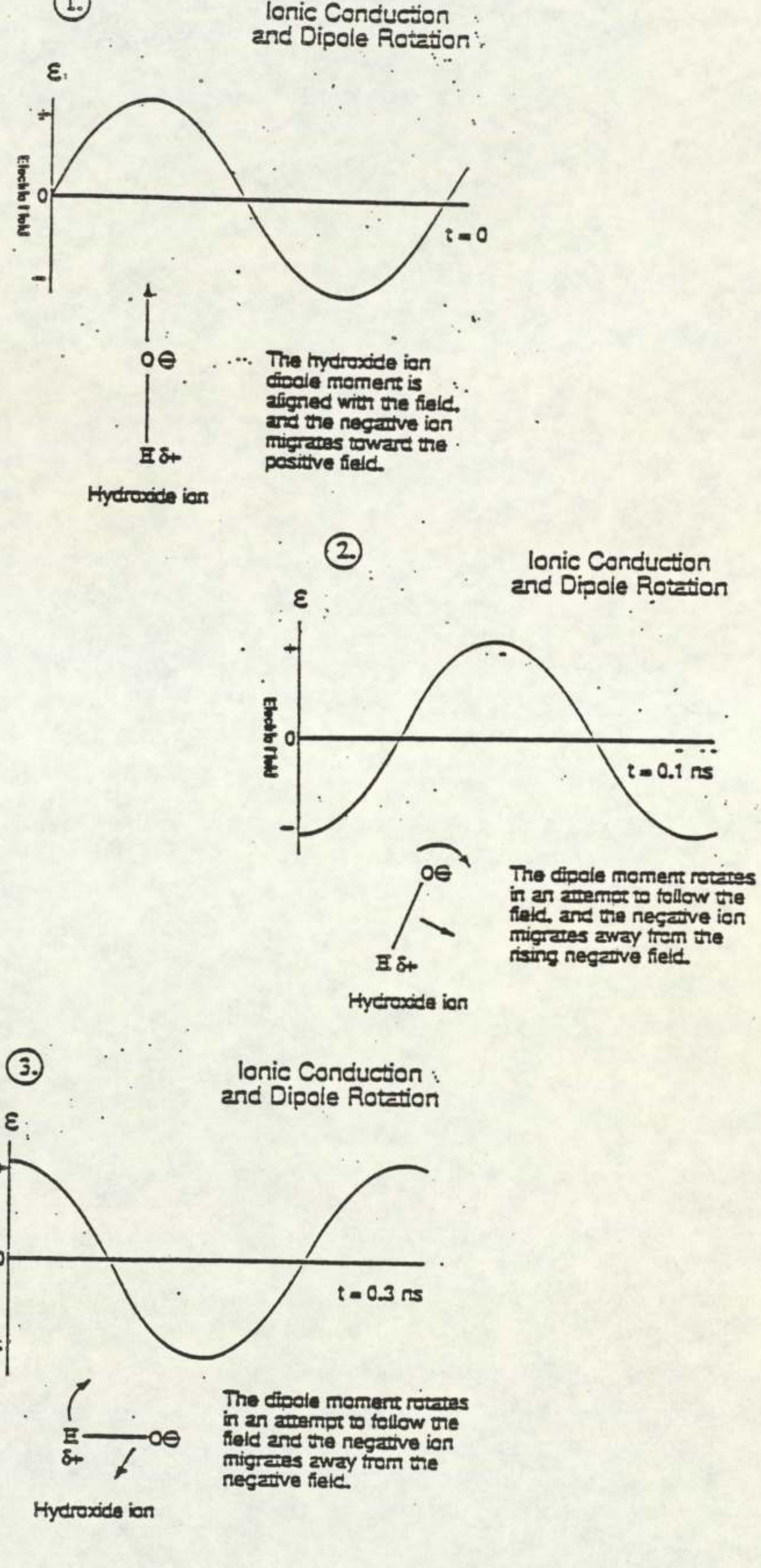
(ii) Infrared Drying:- Rate limiting step is conductance of heat through the sample itself.

(iii) Microwave Drying:- Rate limiting step is transport of the vapour away from the sample.

Oven drying is a slow process, since air is a poor conductor of heat. Microwave and infrared energy are transmitted at the speed of light. But, unlike infrared energy (which relies on conductance of heat through the

FIGURE 5.1

MICROWAVE ELECTRIC FIELD INTERACTION WITH HYDROXIDE ION IN WATER



Ionic Conduction and Dipole Rotation

The hydroxide ion dipole moment is aligned with the field, and the negative ion migrates toward the positive field.

Ionic Conduction and Dipole Rotation

The dipole moment rotates in an attempt to follow the field, and the negative ion migrates away from the rising negative field.

Ionic Conduction and Dipole Rotation

The dipole moment rotates in an attempt to follow the field and the negative ion migrates away from the negative field.

sample), microwaves penetrate some distance into the sample and heat absorbing materials such as styrene. The rate limiting step here is the transport of vapour from the sample. Some heat may be conducted from absorbing liquids (eg styrene) and solids to non-absorbing liquids and solids (eg polyester) in the sample. This residual heat may be important in removing the last traces of moisture from the sample.

Microwave drying almost always leaves the sample cool (below 50°C) after it is dried. This is because microwave energy is not heat but a form of energy which must be absorbed to cause the heating effect. If all the absorbing material (styrene) evaporates, then nothing remains to absorb the microwave energy and it is reflected back out of the cavity.

Therefore, assuming rapid vapour transport from the cavity (as this is rate limiting) microwave analysis should be much faster than oven drying.

Other factors such as sample preparation, the level of power and length of time it is applied will influence accuracy and reproducibility of results - these will be discussed in the following sections.

5.2.2.2 Advantages of Microwave Drying

(i) Dries samples in minutes.

(ii) Does not degrade sample.

(iii) Best precision.

Two instruments were evaluated, the MDS-81 and the AVC-80 supplied by Processing Concepts Limited. The AVC-80 was found to be more appropriate to an R and D environment, rather than production. It was, therefore, the MDS-81 system used in the solids and ash determination of polyester resins.

5.3 Microwave MDS-81; Description, Operation and Accessories

Domestic type microwave ovens supplied commercially have proven to be unsatisfactory for laboratory use due to early failures of the microwave source (magnetron) and uneven distribution of microwave energy ("hot spots"). The MDS-81 magnetron is protected from overheating caused by reflected microwave energy. This ensures long magnetron life and provides consistent, reproducible power output test after test, regardless of sample size. The microwave energy is distributed evenly throughout the oven cavity to provide constant repeatable conditions.

The Microwave MDS-81 (refer to figure 5.2) has the following features and accessories:-

(i) Time and microwave power (the two variables on the instrument) can be independently programmed in one second and one per cent increments for precise control. At 100 per cent power, the MDS-81 delivers 600 watts of microwave energy to the sample.

(ii) The MDS-81 is programmable in up to nine stages. Time and power selections are independently programmed for each stage and the user is continually up-dated on the readout during operation.

(iii) A variable speed exhaust system permits high air flow through the oven cavity to aid in drying (by removing vapour from the sample, see section 5.2.2.1) and ashing.

(iv) A turntable rotates the samples at 6 rpm under a distributed microwave field.

(v) Ten cms diameter glass fibre sample pads are used to hold the sample.

(vi) A thermapad can be used to provide thermal energy in addition to microwave energy and thus ensure the removal of the last traces of solvent. The thermapad is a rubber pad containing ceramic material that will absorb microwave energy. The ceramic content is such that the pad will reach a predetermined temperature (for polyester solids this is 120°C). The pad is heated up by the microwave whilst the samples are being weighed and the temperature is thereafter maintained by the microwave energy used during sample analysis.

The thermapads are the same shape and size as the sample pads.

(vii) When samples require ash analysis, the turntable is replaced with a muffle furnace (refer to figure 5.3). Samples are heated in an enclosed chamber, 65 mm in diameter and 85 mm high, located inside the insulating ceramic of the furnace. A door piece is used to gain access to the heating chamber. The ceramic material inside the furnace absorbs microwave energy and temperature of up to 1200°C can be reached. However, the operating temperature for polyester ash is 800°C ± 5°C and is maintained using a temperature controller. Pre-heating the furnace will minimise analysis times.

(viii) Crucibles made of a quartz fibre material are used to measure ash content.

5.4 Microwave Determination of the Solids Content of BIP Polyester Resins

NB At the time of the trials, the author and suppliers of the microwave (Processing Concepts Limited) were unaware of any work related to the determination of the microwave solids content of polyester resins.

Microwave analysis was evaluated in the hope that such a technique would be more reproducible and less time consuming. However, any new test method would have to correlate with results from the oven test, to avoid the need for changing the BIP product specifications.

5.4.1 Establishing a Test Procedure

There are three main variables that can influence the accuracy and reproducibility of the microwave results:-

(i) Sample Preparation
(ii) Time Under Test
(iii) Power Level.

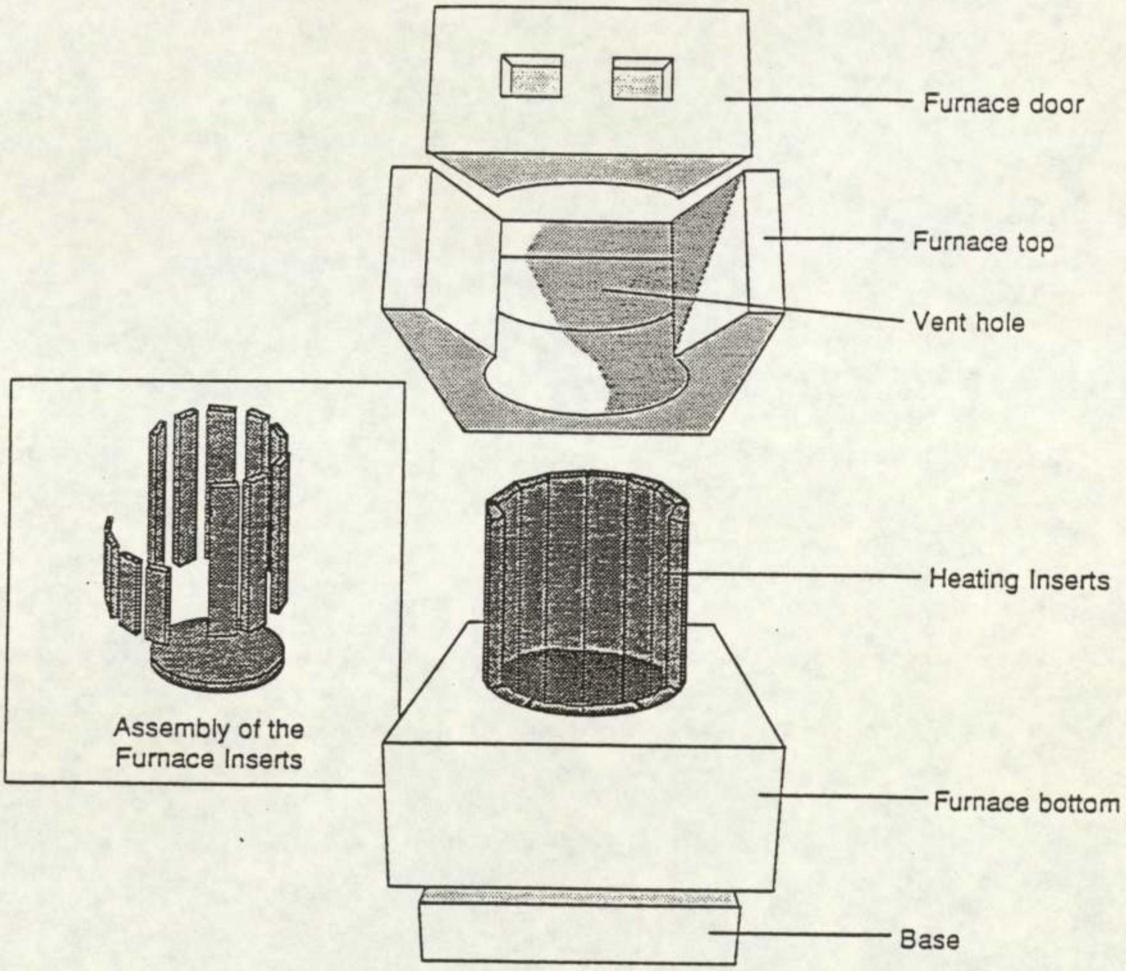
Each will be discussed separately:

Figure 5.2: MDS-81 Microwave

Figure 5.3: **Muffle Furnace**

SCHEMATIC DIAGRAM OF THE MUFFLE FURNACE

Assembly of the Muffle Furnace



5.4.1.1 Sample Preparation and Analysis

There are several ways of applying the resin to the sample pads, bearing in mind the high viscosity of most resins:-

(i) Spread evenly over the surface of the pad.

(ii) Spiral stream from the centre.

(iii) Puddle.

Initial trials[8] had shown that "puddling" the sample was the best way to apply the resin to the sample pads. However, the use of a thermapad changed conditions and has shown spreading the resin evenly over the surface of the sample pads to be the best application method.

A standard procedure for sample preparation and analysis was established for all the resins examined during the trials.

(i) Weigh out three sample pads together (w_1).

(ii) Weigh 2 g ± 0.005 g of resin onto the pads and spread evenly over the surface. Re-weigh the pads (w_2).

(iii) Take the lower pad and place it on top of the sample to form a "sandwich".

(iv) Place the sample in the microwave for the required time and power level (see section 5.4.1.2).

(v) When the sample run is finished, remove the sample pads from the microwave and re-weigh (w_3).

From these results, the solid resin yield may be calculated:-

$$\text{Solid Resin Yield} = \frac{w_3 - w_1}{w_2 - w_1} \times 100\% \qquad (5.1)$$

The result is recorded as the mean of two determinations provided that the two determinations do not differ by more than 1%.

Note: (i) A 2 g sample was selected to give a direct comparison with the traditional oven method (see section 4).

(ii) Three sample pads were used so that two may form a base, to prevent loss of resin through leakage from the pads.

5.4.1.1.1 The Use of a Thermapad

Preliminary investigations proved that microwave power alone was not sufficient to provide results similar to those obtained from the oven method. Whether in fact these results are correct is not an issue here.

eg Low power levels resulted in high solids results, whereas high power levels were seen to char the resin. When the resin became charred, the results were not reproducible, due to degradation of the polyester.

Therefore, a thermapad (see section 5.3) was used to help establish a test procedure. The use of thermal energy (120°C from the thermapad) in addition to microwave energy was seen to yield the expected results.

Thermapads capable of reaching different temperatures are available. A 120°C thermapad was used to analyse polyesters, since a higher temperature thermapad used in addition to microwave energy may be too fierce and sample degradation may occur. (The conventional oven method operates at 150°C of thermal energy.)

When samples have been prepared (see section 5.4.1.1) they are placed onto pre-warmed thermapads in the microwave and analysed.

5.4.1.2 Optimisation of the Microwave Equipment

The microwave equipment has the facility to enter nine different programs of run time and power level which run in sequence 1 to 9 (see section 5.3). However, during the trials only two programs were required:-

P1 100%	T1 5 minutes
P2 x %	T2 5 minutes.

The first program is run while weighing out the samples, to ensure the thermapads reach 120°C before analysis. When the first program is complete, the samples are introduced and the second program started.

A standard run time of 5 minutes (T2) was used in the second program. However, different resins were seen to require different power levels and so P2 depends on resin type.

Note: For resins whose solids content is not achieved when P2 is 100%, T2 is extended.

5.4.1.2.1 Establishing Suitable Power Levels

To determine the power required (P2) to analyse a particular resin type, plots of % power *vs* % residue for fixed drying times (ie drying curves) were produced. The oven result (pre-determined by the control laboratory) was incorporated into the plot and the power level determined by the intercept between the oven result and the drying curve.

As the trials became more advanced it became unnecessary to produce drying curves for each resin type, ie the solids content of the untested resins may be the same or very similar to resins whose power level had already been established. In this case, this power level was used and adjusted (if necessary) depending on the solids result.

After optimising the microwave procedure, several batches of each resin were examined to ensure that suitable conditions had been established. In each case the microwave results were compared with the oven solids result from the control laboratory.

5.4.1.3 Reproducibility

Reproducibility of the new technique required examination, since solids analysis is a quality control test. Therefore, a new test should show an improvement in reproducibility when compared with the conventional oven method (see section 5.1).

When the microwave had been optimised for all BIP polyester resins, reproducibility was investigated:

Several resins were chosen at random and the reproducibility determined by analysing 10 duplicate samples for each resin. Standard deviation was used to indicate variation within the test procedure. The results were then compared with those from the oven method.

5.4.1.4 Comparison of the Microwave and Oven Solids Test Procedure

When the microwave test method had been established, the two test procedures were compared by analysing the microwave and oven solids content of resins entering the control laboratory on a daily basis.

5.4.2 **Results and Discussion**

5.4.2.1 Initial Commissioning

A series of resins (see Table 5.1) were selected to cover the solids content range of BIP polyester resins, ie from the lowest solids polyester (resin Q = 55% solids) to the highest (resin A = 75% solids). Successful analysis of these resins has enabled determination of the remainder of the polyester range (see Table 5.2).

Sixteen resins were initially studied and the microwave technique optimised for each (see section 5.4.1.2):

Table 5.1: Microwave Conditions Used During the Initial Analysis of BIP Polyester Resins

Resin Type	Power (P2) %	Run Time (T2) mins	Product Specification %
AY	68	5	60 ± 2
AM	52	5	70 ± 2
Q	98	5	55 ± 2
A	100	5	75 ± 2
AB	67	5	65.5 ± 2
B	80	5	66 ± 2
AG	65	5	70 ± 2
AH	60	5	73 ± 2
W	95	5	58.5 ± 2
D	65	5	61.5 ± 1.5
R	98	5	55 ± 2
BH	100	10	56 ± 2
Z	100	5	61 ± 2
AK	70	5	66.5 ± 2
AX	75	5	62 ± 1.5
BF	70	5	65.5 ± 1.5

Note: The results obtained in Table 5.1 were achieved using a single thermapad. A second thermapad was obtained to enable duplicate analysis. However, the microwave conditions established in Table 5.1 would need adjustment to compensate for the change in test conditions with a second sample present, ie a slight increase in power or time may be necessary (see Table 5.2).

Program one was standard for each resin studied, to warm the thermapad (see section 5.4.1.2), and ran whilst the samples were being weighed to reduce overall run times.

As many stages as possible were standardised to make the procedure easier to follow and so reduce the possibility of experimental error. In fact, of the 16 polyesters studied, all the resins were analysed using a standard sample preparation (see section 5.4.1.1), pre-start preparation (ie warming of the thermapad) and run time (with the exception of resin BH whose run time was 10 minutes). However, the power levels were seen to vary for many of the resins studied:

The power levels are obtained from the intercept of the microwave drying curve with the oven solids result. Appendix 1 shows the intercept on the drying curves for many of the resins reported in Table 5.1 (see figures 1 to 9). The power level may require fine tuning, as experience is obtained, since the position of the intercept will depend on the accuracy of the oven result.

Example 1: Resin D (see figure 7 of Appendix 1)

The intercept of the drying curve and oven result is seen at a power level of approximately 64%. In fact, a 65% power level was found to produce the desired results (see Table 9 of Appendix 1), eg batch 71 microwave and oven solids = 62.6%. Figure 7 shows three distinct stages on the drying curve:

50% to 65% power - a sharp reduction in weight is seen due to evaporation of styrene

65% to 70% power - constant weight is achieved and probably relates to the solid content of the sample

70% to 80% power - further reduction in weight due to sample degradation

Some of the drying curves do not show a plateau and an accurate power level is essential (see figure 5). In this case a slight discrepancy in power will change the measured solids content and reproducibility may be poor.

Example 2: Resin AY (see figure 1 of Appendix 1)

A 68% power level (*cf* the intercept at 69%) provided a good correlation between the microwave and oven solids test methods (see Table 1), eg batch 442: microwave solids = 59.9% *cf* oven solids = 60.0%. The exception is batch 441 where the microwave solids is 60.86% *cf* oven solids of 59.6%. However, when the oven result was repeated, a solids content of 60.54% was achieved.

The repeat result is nearer the microwave solids value, confirming the inaccurate nature of the oven solids method.

A similar trend was observed for other resins in the series, ie the power level used was seen as the intercept or very close to it and any differences between the two techniques were found to be attributable to inaccuracies in the oven method. In all cases, repeat oven tests showed an improved correlation between the two techniques and so question the accuracy of the oven solids test method.

The exception of the series was resin A, where the drying curve (refer to figure 8 of Appendix 1) shows the microwave solids to be 1% higher than the oven solids at 100% power, eg batch 142: microwave solids 77.0% *cf* oven solids 76.0% (see Table 11). Extended run times of up to 30 minutes did not significantly reduce the measured solids content. Therefore, either the microwave technique is unsuitable for the analysis of this resin or the oven result is inaccurate.

Note: The problems encountered with this resin were eliminated when duplicate analysis was carried out (see Table 5.2). No explanation for the initial discrepancies can be proposed.

5.4.2.2 Duplicate Analysis

The arrival of the second thermapad coincided with the need to examine the remainder of the polyester resins. In addition to analysing untested resins, the resins from Table 5.1 were re-examined to determine what effect a second sample would have on power level and run time. The conditions used to determine the entire BIP polyester range are recorded in Table 5.2, and are in fact the conditions used in the new microwave test procedure (refer to Appendix 1a).

Table 5.2 shows that the microwave conditions differ between duplicate and single sample analysis (see Table 5.1).

eg	resin AY	Power (%)	Time (mins)
	single analysis	68	5
	duplicate analysis	95	5

This trend is repeated for all the resins analysed in Table 5.1. The need for an increase in power is due to the introduction of a second thermapad (requiring microwave energy to heat and maintain at 120°C) and sample (also requiring microwave energy to remove styrene). The extra demand for microwave energy requires an increase of power. In many cases 100% power is used and the run time extended to provide the extra microwave energy.

5.4.2.3 Reproducibility

Ten resins were selected at random from the BIP polyester range and reproducibility examined by determination of the standard deviation of ten duplicate samples for each resin. The results are recorded in Table 5.3.

An improvement in reproducibility is observed for resins analysed with the new microwave test method compared with the conventional oven method:

eg Microwave analysis of resins AY and Q yields standard deviations of 0.30 and 0.25, respectively - compared with 0.42 and 0.52 from oven analysis.

Experience of oven analysis would suggest a standard deviation of approximately 0.5, since the variation in solids can be ± 1% in a ± 2% specification[8] (see Table 17 of Appendix 1). All resins analysed by the microwave test procedure are within this standard deviation. Resins V and AP produce results similar to those expected from the oven method (ie 0.49 and 0.42, respectively). However, further experience with the test procedure should improve this situation, since a new technique is being compared with an established test method. Although the standard deviations are higher than

Table 5.2: Microwave Conditions Used in the Determination of Solid Resin Yield

Resin Type	Run Time (T2) mins	Power (P2) %	Product Specification %
A	15	100	75 ± 2
B	5	80	66 ± 2
C	5	83	62 ± 2
D	5	70	61.5 ± 1.5
E	12	100	58 ± 2
F	12	100	62 - 66
G	10	100	58 ± 2
H	15	100	75 ± 2
I	5	50	59 ± 2
J	10	100	58 ± 2
K	10	100	55 ± 2
L	5	100	55 ± 2
M	5	95	57 ± 2
N	10	100	56 ± 2
O	10	98	62 ± 2
P	5	100	63 ± 2
Q	10	100	55 ± 2
R	10	100	55 ± 2
S	7	100	56 ± 2
T	12	100	56 ± 2
U	10	100	69 ± 2
V	5	100	62 ± 2
W	5	100	58.5 ± 2
X	7	100	59 ± 3
Y	10	100	60 ± 2
Z	5	100	61 ± 2
AA	5	80	72 ± 2
AB	5	80	65.5 ± 2
AC	5	80	64 - 67
AD	5	60	65.5 - 69.5

Table 5.2 (continued)

Resin Type	Run Time (T2) mins	Power (P2) %	Product Specification %
AE	5	100	56 ± 2
AF	10	100	68.5 - 72.5
AG	5	70	70 ± 2
AH	5	65	73 ± 2
AI	5	90	68.5 - 72.5
AJ	5	80	62 ± 2
AK	5	70	66.5 ± 2
AL	5	100	70 ± 2
AM	10	65	70 ± 2
AN	5	85	68 ± 2
AO	5	65	70 ± 2
AP	5	100	67 ± 2
AQ	20	75	72 - 76
AR	7	100	63 ± 2
AS	10	100	60.5 ± 2
AT	10	100	59.5 - 63.5
AU	5	100	59.5 - 63.5
AV	15	100	56 ± 2
AW	5	100	72 ± 2
AX	5	85	62 ± 1.5
AY	5	95	60 ± 2
AZ	10	95	64 ± 2
BA	7	100	54 ± 2
BB	5	100	61.5 ± 2
BC	15	80	63 ± 2.5
BD	5	100	55 ± 2
BE	5	70	65.5 ± 1.5
BF	5	90	65.5 ± 1.5
BG	5	100	62 ± 2
BH	10	100	56 ± 2
BI	5	100	63 ± 2.5

Table 5.3: **Determination of Reproducibility for the Microwave Test Procedure**

Resin Type	Microwave ($\sigma n-1$)	Oven ($\sigma n-1$)
AM	0.25	
AG	0.37	
AY	0.30	0.42
Q	0.25	0.52
W	0.37	
AX	0.32	
V	0.49	
AP	0.42	
BE	0.27	

anticipated, they appear no worse than the oven method. There is, therefore, an overall improvement in reproducibility when determining the solid resin yield of polyester resins via microwave analysis rather than the conventional oven procedure.

5.4.2.4 A Comparison of the Microwave and Oven Solids Test Procedures

The two test procedures were compared by analysing the microwave and oven solids content of resins entering the control lab on a daily basis.
- refer to Table 5.4.

A good agreement is observed between the two test procedures (Table 5.4). All the results correlate to within ± 1.0% of each test procedure. In fact, most compare to within ± 0.3%. Although there is some variation between the two techniques, all the results are within product specification for each resin. Since the reproducibility of the microwave test is better than the oven method, it can be inferred that the microwave results are more accurate.

Table 5.4: A Comparison of the Solids Content between the Microwave and Oven Test Procedures

Resin	Batch No	Microwave Solids (%)	Oven Solids (%)	Difference (%)
AH	946	73.8	73.3	+ 0.5
R	146	55.7	55.2	+ 0.5
AH	947	73.0	73.3	- 0.3
BF	160	67.0	66.4	+ 0.6
BF	159	65.3	65.2	+ 0.1
B	239	66.7	66.1	+ 0.6
AB	951	66.8	66.8	Zero
BF	160B	65.1	66.1	- 1.0
AH	948	73.5	74.0	- 0.5
AH	949	73.5	73.1	+ 0.4
AM	435	70.5	70.3	+ 0.2
AB	952	66.2	65.6	+ 0.6
AG	397	70.5	71.0	- 0.5
AT	120	63.2	62.4	+ 0.8
AH	955	74.2	74.3	- 0.1
AW	277	70.4	70.7	- 0.3
AY	519	61.2	61.0	+ 0.2
AH	953	74.2	73.8	+0.4
Z	202	61.1	61.1	Zero
AG	389	71.2	70.7	+ 0.5
AB	954	67.1	66.7	+ 0.4
Q	562	55.9	55.4	+ 0.5
AH	954	74.5	73.7	+ 0.8
AH	950	73.9	72.9	+ 1.0
AH	951	73.9	74.2	- 0.3
AH	952	73.8	74.3	- 0.5
AB	953	66.2	66.4	- 0.2
AY	520	60.6	60.7	- 0.1
AH	956	73.8	74.0	- 0.2
AM	436	70.1	70.0	+ 0.1
AG	402	71.1	71.0	+ 0.1
Q	567	55.1	54.9	+ 0.2
AG	403	70.9	70.6	+ 0.3
AW	278	70.2	70.3	- 0.1
AH	958	73.2	73.3	- 0.1
AG	404	71.1	70.7	+ 0.4
AG	405	70.9	70.6	+ 0.3
AY	521	61.1	60.7	+ 0.4

Note + denotes microwave solids higher than oven solids
- denotes microwave solids lower than oven solids.

The comparison of two different test procedures would not be expected to produce the same results, since different techniques of analysis may introduce different experimental errors.

5.4.3 Conclusions

1 A Microwave test procedure has been successfully developed to determine the solid resin yield of BIP Polyester resins.

2 The new test method is:
  (i) more reproducible
  (ii) quicker
than the conventional oven technique.

3 Microwave solids analysis is, therefore, a better quality control test than oven solids (due to improved reproducibility).

4 Plant productivity may be improved as microwave analysis is quicker and therefore will reduce hold-ups associated with awaiting results.

5.4.4 Recommendation

1 Replace the oven method with the new microwave test procedure (see Appendix 1a) to determine the solid resin yield of BIP polyester resins.

5.5 Determination of the Microwave Ash Content of BIP Polyester Resins

The MDS-81 microwave system can also be used to determine the ash content of polyester resins. The traditional ashing procedure is very time consuming (see section 5.1) and therefore unsuitable for on-line testing. The microwave was evaluated to establish a new test procedure that will reduce the analysis time.

5.5.1 Ashing Requirements

Only six of the BIP range of polyesters require analysis of their ash content. These are resins that contain inorganic fillers/pigments. Some of these additives impart various properties to the resins, eg fire resistance, and so their content will require measurement.

Other resins are used to provide the outer skin of boat hulls. Lloyd's Register stipulates the amount of inorganic fillers/pigments to be contained in the resin and the ash test is used to monitor this level.

5.5.2 Establishing a Test Procedure

A muffle furnace at 800°C is proposed (see section 5.3 for a description of the equipment and mode of operation) so that the principles of the test are very similar to the traditional ash procedure (see section 4).

5.5.2.1 Setting Up the Microwave

(see section 5.3 for a description of the equipment)

(i) Remove the turntable, insert the muffle furnace (see figure (5.3)) and set the exhaust fan to maximum.

(ii) Programme the thermocouple to control the muffle at 800°C (see Appendix 1c). This temperature was chosen for direct comparison with the traditional method (see Chapter 4).

(iii) Run the microwave using 100% power for approximately thirty minutes, ie until 800°C is reached.

(iv) Samples may be prepared while the muffle is heating up. The ashing temperature of 800°C is maintained during sample analysis. Subsequent testing time will be reduced since reheating of the muffle is not required.

(v) When analysis is complete, the muffle furnace may be removed within minutes (as the blocks cool rapidly) and the system returned to solids measurement almost immediately.

Note: The use of a second microwave will eliminate the problem of changing between solids and ash (see section 5.6).

5.5.2.2 Sample Preparation and Analysis

Quartz fibre sample pads or crucibles are available for ashing. The quartz fibre crucibles proved easier to use, were re-usable and were,therefore, used during the trials. The lifetime of the crucibles may be extended with the introduction of a protective base (also quartz fibre).

The following sample preparation and analysis became standard throughout the trials:-

(i) Accurately weigh and clean crucible and two disposable discs.

(ii) Place one of the discs in the crucible (to provide a base) and weigh 5 g ± 5 mg of sample into the crucible. The second disc is gently placed onto the sample to provide a lid (and prevent physical loss of ash).

(iii) The sample is ashed by placing the crucible into the muffle at 800°C for the required time.

(iv) Remove the crucible from the muffle and re-weigh the crucible, two disposable discs and residue.

From these results the ash content can be calculated:-

$$\%\ \text{Ash w/w} = \frac{100 \times R}{W} \qquad (5.2)$$

where:

R = weight of residue (g)

W = weight of sample (g).

Note: A 5 g sample is used to compare directly with the oven method (see Chapter 4).

5.5.2.3 Establishing a Standard Run Time

All samples undergo the same preparation procedure and are analysed using 100% microwave power. The run time is, therefore, the only variable:

The microwave ash results were compared with those from the traditional method and the run time adjusted until a reasonable agreement was achieved between the two test methods, ie ± 0.2%. The effect of duplicate sample analysis on run time was also examined.

5.5.3 **Results and Discussion**

For each resin studied, a run time of 20 minutes for single samples provided comparable results, ie showed a good correlation with the traditional method. However, a run time of 20 minutes was insufficient for the analysis of duplicate samples. This was due to the temperature lost by the muffle as the two samples were introduced. The muffle rapidly loses heat when the port door is opened. The increase in sample number results in the door being open for a greater length of time, thus increasing the heat loss. The more heat lost by the muffle, the greater is the time taken to reach 800°C and the longer the run time. A 25-minute run-time was found to be suitable for duplicate samples.

The following run times were used, irrespective of resin type:-

(i) single sample for 20 minutes

(ii) duplicated samples for 25 minutes.

Consultation with laboratory personnel showed that analysis of two samples would cope with the production schedule.

Standard run times have completed the preparation of a new microwave test procedure (see Appendix 1c) and the following results obtained using the new test method.

Since only six of the BIP polyester resins require analysis of their ash content, each will be examined individually.

5.5.3.1 Resin AH (refer to Table 1 of Appendix 1b for the results)

All the batches studied showed a very good agreement between the microwave result and the traditional result. The greatest deviation between the two test methods was 0.3% for batch 859 (FI0). However, the microwave result was drawn from a good agreement between a duplicate sample, ie 13.61% and 13.72%. Such a good agreement would indicate that the microwave result is more accurate. The argument is strengthened by the fact that the traditional method may be more susceptible than the microwave to experimental error, eg decomposition of the resin with a bunsen burner may involve some physical loss (refer to section 4).

The majority of batches analysed showed an agreement between the two test methods of ± 0.1%. The agreement between duplicate samples was also very good:-

eg

	Microwave (%)			Traditional oven (%)
	(i)	(ii)	x	
Batch 861 (FIO)	13.68	13.63	13.66	13.6

The analysis of single samples (using a 20-minute run time cf 25 minutes for a duplicate) shows a good agreement with both the traditional result and the duplicate result:-

eg

	Microwave (%)		Traditional oven (%)
	single	duplicate	
Batch 846	14.05	14.02	14.0

5.5.3.2 Resin AG (refer to Table 2 of Appendix 1b for the results)

All the results obtained by microwave technique (with the exception of batch no 117 (FIO)) show a good agreement between the two test methods, ie within ± 0.2%. The traditional result obtained for batch no 117 (FIO) is 2.0%. This is thought to be inaccurate since the final oven ash was 2.6%. The adjustment between the FIO and final tests was 400g of inhibitor. It is, therefore, extremely unlikely that such a small adjustment on a one tonne batch will change the ash content by 0.6%! Therefore, the microwave result of 2.71% (cf 2.6% final oven ash) is thought to be more accurate.

Agreement between duplicate results is good (eg batch 118 microwave solids 2.64% and 2.54%), as is the agreement between single samples (20-minute run time) and the traditional ash (eg batch 70 microwave ash = 2.42% cf oven ash = 2.48%).

5.5.3.3 Resin A (refer to Table 3 of Appendix 1b for the results)

Agreement between the two test methods is again very good, ie microwave result = oven result ± 0.3%. It is unlikely that two different test methods would yield exactly the same result.

Batch no 139 is outside the specifications when analysed by the traditional method, ie 26.3% (specification = 26.5% - 29.5%), but in specification with microwave analysis, ie 26.5%. Both microwave test procedures (single sample run time = 20 minutes and duplicate run time = 25 minutes) yield a solids content of 26.5%. Agreement between the duplicate samples is good, as is that between the single run and the duplicate. These results would indicate that the microwave test procedure is more accurate.

Other batches show good agreement between duplicates:-

eg

batch no 138 26.66% and 26.71% (oven = 26.97%).

The difference between the two test methods is thought to to be caused by inaccuracies in the traditional ashing procedure. Traditional ashing involves more stages of analysis, thus increasing the probability of introducing experimental error.

5.5.3.4 Resin AW (refer to Table 4 of Appendix 1b for the results)

Both test methods are seen to yield ash results to within ± 0.2% of each other. Duplicate reproducibility was again good:-

eg

Batch no	Microwave ash (%)			Traditional ash (%)
	(i)	(ii)	x	
267	19.90	19.92	19.91	20.02
270	20.99	20.98	20.99	20.90

Single sample analysis also produced encouraging results:-

eg

batch no 271 21.16% (oven = 21.14%).

5.5.3.5 Resin AJ (refer to Table 5 of Appendix 1b for the results)

Accurate and reproducible results are required for this resin, since the specification is very tight, ie 1.5% - 2.1%.

Agreement between the two test methods for both procedures (ie single and duplicate run times) is good:-

eg

Batch no	Microwave ash (%)			Traditional ash (%)
	(i)	(ii)	x	
189	1.62	1.60	1.61	1.7
190	1.56	-	-	1.59

All the batches (with the exception of batches 184 and 185) were within ± 0.16% for each test method.

Microwave analysis of batch 185 yielded an ash content of 1.82% (0.31% higher than the traditional result of 1.51%). However, when the run time was extended to 30 minutes the microwave ash content was 1.78%. This value is very similar to that obtained with a 20-minute run time (1.82%), indicating that the traditional result was inaccurate (ie the resin had reached constant ash after 20 minutes). The traditional result may be low due to the inaccuracies associated with this method, eg there may have been some physical loss during the decomposition stage.

Batch number 184 showed a microwave ash content of 1.72% and 1.68%, but a traditional ash of 2.0%. Since the agreement between the duplicate samples is good, it can be assumed that the traditional result is inaccurate. Such a discrepancy is alarming, since the difference between the two test methods accounts for 50% of the specification.

5.5.3.6 Resin AK (refer to Table 6 of Appendix 1b for the results)

Excellent agreement between the two test methods and between duplicate and single runs, indicates that the test procedure established in Appendix 1c is suitable for the ash analysis of this resin:-

eg

Batch no	Microwave ash (%)			Traditional ash (%)
	(i)	(ii)	x	
81	13.58	13.58	13.58	13.6
88	13.51	13.42	13.47	13.4
88	13.48	-	13.48	13.4

In fact, all BIP resins (requiring ash content analysis) can be successfully ashed using the new microwave test procedure in Appendix 1c.

5.5.3.7 Simultaneous Analysis of Different Resin Types (refer to Table 7 of Appendix 1b for the results)

Various combinations of different resin types were analysed to simulate the conditions experienced in the day-to-day running of the control laboratory. In some cases different resins will require determination of their ash content at approximately the same time. Several combinations of resin were analysed using a 25-minute run time (refer to Table 7). Only two resins per run were analysed, since the short run times should cope with the production schedule.

All the results show both test methods to agree to within ± 0.2% (with the exception of Resin AH/838 and Resin A/138). The discrepancy (± 0.4%) between the test methods for the two resins mentioned above may be explained:-

(i)	AH/838	Microwave ash (%)	Traditional ash (%)
		14.11	13.70

The FIO test (ie the test prior to submission of the final sample) showed an ash content of 14.0% (cf microwave ash = 14.11%). Since the adjustment between the two samples was only 200g of inhibitor, it appears unlikely that the ash content should change. (Particularly since the adjustment was made to a one tonne batch.) The final traditional ash is, therefore, thought to be inaccurate.

(ii)	A/138	Microwave ash (%)	Traditional ash (%)
		26.55	26.97

Further microwave determinations have shown the ash content of this batch of resin to be 26.6% ± 0.05% (on three separate occasions). It is again the traditional ash result that appears inaccurate.

5.5.4 Conclusions

1 A new microwave test procedure has been established to determine the ash content of BIP polyester resins.

2 The new test procedure is:-
  (i) quicker
  (ii) more accurate
  than the conventional method.

3 Microwave ashing is, therefore, a more suitable quality control test (due to improved accuracy).

4 Faster analysis will reduce the hold-ups associated with awaiting results and improve plant productivity.

5.5.5 Recommendation

1 Replace the traditional method with the new microwave test procedure to analyse the ash content of BIP polyester resins.

5.6 Equipment Provision

Using a single microwave oven would result in continual changing of the instrument from solids to ash and vice versa. This will cause numerous problems:-

eg

(i) The time savings associated with microwave analysis will not be as great if the instrument is continually changed to accommodate both test procedures. When changing from solids to ash, at least 30 minutes is required to heat the furnace to 800°C, resulting in an increase of analysis time for the ash test. Problems may also be encountered when changing from ash to solids. For example, the removal of a muffle furnace at 800°C from the microwave may provide an element of danger to laboratory personnel. The removal of the muffle furnace will also incur a time delay to the solids test.

This increase in testing time for the solids and ash tests will reduce the increase in plant availability possible from microwave analysis.

(ii) A single instrument may be incapable of coping with the production schedule.

(iii) Simultaneous analysis of solids and ash would be impossible. This will increase analysis times over and beyond the time delays discussed in (i).

However, the purchase of a second instrument may help to rectify the situation:

eg

(i) There would be no change-over required between the solids and ash test procedures. This will prevent the time delays of such a system and therefore provide the increase in productivity possible from microwave analysis, ie microwave testing will reduce the hold-ups associated with awaiting oven solids and ash results.

(ii) A second microwave would provide each test procedure with its own dedicated instrument. This will enable simultaneous analysis and provide the facility to cope with the production schedule.

(iii) The use of a second microwave will provide a back up. Since each instrument is capable of solids and ash analysis, any failure to either instrument would be accommodated, ie one instrument should cope in the short term with the solids and ash tests while the second instrument is repaired.

The clear benefits of a second microwave led to the purchase of another instrument. BIP now have two microwaves, one instrument dedicated to each test.

5.7 The Financial Advantages Associated with Microwave Solids and Ash

5.7.1 Introduction

The microwave is to be used as a replacement for the current oven solids/ash content of polyester resins. One of the main advantages associated with the microwave is the time saved during testing:

ie 1 hour per test for solids

and, 1.5 hours per test for ash.

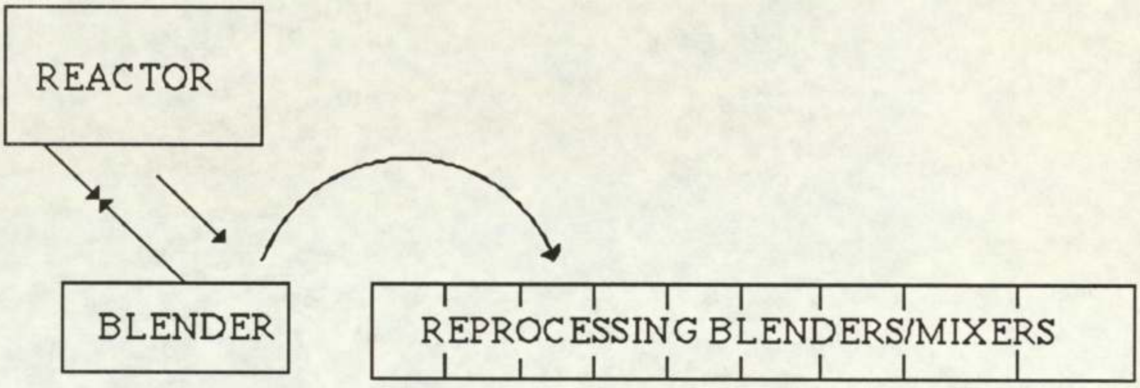
The time saved can then be related to the plant by reducing the total processing time for each batch of resin, thus providing the potential for an increase in production. The increased production will be related to annual contribution* to determine the financial advantages associated with the microwave. Although the microwave could be used to increase production, factors such as increased base resin production required to meet the increase in potential will need consideration. This and others (eg plant capacity, labour, demand from the market) will be discussed in the following sections.

* Contribution = Selling Price - [Raw Material + Packaging Costs]

5.7.1.1 The Limiting Step: Scenario I

The limiting step to increasing production would be the manufacture of base resin.

Figure 5.4:



The resin is held in the associated blender whilst awaiting ash or solid content results. Therefore, the reduction in testing time will enable faster transfer of resin to the various blenders to obtain the finished product. Faster release from the reactor/blender will enable the next batch to be charged, thus reducing processing times. However, the reaction times will remain the same and must be considered when estimating increased production.

The following assumptions have been made in estimating the potential increase in contribution from microwave testing:-

(i) Market demand exists for increased resin manufacture.

(ii) The plant could cope with an increase in output, ie no shortage of labour nor any change in equipment failure rates/maintenance.

Note: Increased production will be related to plant capacity (see section 5.7.4)

5.7.2 Solids

The increase in potential annual production and ultimately contribution is calculated for each resin in Table 5.2 when microwave solids replace oven solids:

If:- α = Processing time (hours), ie charging, reaction time and cooling/blending.
β = Batch size (tonnes).
χ = Number of batches manufactured from March 1989 to April 1990.
∂ = Number of re-tests required per year.
ε = Processing time using microwave solids.
θ = Annual time saving (hours) from microwave analysis in relation to χ and ∂.
γ = Potential increase in annual production (tonnes) when microwave solids replaces oven solids.
H = Contribution (£/tonne) = Selling Price - [Raw Material + Packaging Costs].

Then:-

$$\varepsilon = (\alpha - 2) \qquad (5.3)$$

ie the batch time is reduced by two hours when microwave solids replace oven solids, and:-

$$\gamma = \frac{\theta}{\varepsilon} \times \beta \qquad (5.4)$$

$$\text{where } \theta = (\chi \times 2) + (\partial \times 1) \qquad (5.4.1)$$

when the time saving is taken as two hours per batch (ie which are saved on both FIO and Final tests) unless a re-test is required, in which case add one hour for each re-test,

and

$$\textbf{Total Contribution (£)} = \gamma \times H \qquad (5.5)$$

when substituting for each resin in equations 5.3 to 5.5 an increase in annual contribution of **£477,177** is calculated.

However, this figure will be incorrect if the increased potential for base resin cannot be achieved by the capacity of the plant (see section 5.7.4).

5.7.3 Ash

The potential increase in annual production and hence contribution is calculated for the resins in Table 5.3 when microwave ashing replaces traditional ashing:

If:-

α = Batch time (hours) using traditional analysis, ie charging blending, running off and testing.
ε = Batch time (hours) using microwave analysis.
χ = Number of batches manufactured from March 1989 to April 1990.
Π = Annual accumulated batch time (hours) for traditional analysis.
ω = Annual accumulated batch time (hours) for microwave analysis.
θ = Annual accumulated time saving (hours).
ψ = Potential increase in annual production (tonnes).
H = Contribution (£/tonne).
ß = Batch size (tonnes)

Then:-

$$\varepsilon = \alpha - 3 \qquad (5.6)$$

ie The batch processing time is reduced by 3 hours since 1.5 hours is saved during the testing of FIO and Final samples. (Note: no ash re-tests were required for any of the resins studied.)

$$\theta = \Pi - \omega \qquad (5.7)$$

where:-

$$\Pi = \alpha \times \chi \qquad (5.7.1)$$

and:-

$$\omega = \varepsilon \times \chi \qquad (5.7.2)$$

$$\psi = \frac{\theta}{\varepsilon} \times \beta \qquad (5.8)$$

Substituting into equation 5.5:-

Total Contribution (£) = $\psi \times H$.

An annual increase in contribution of **£361,983** is calculated when microwave replaces traditional ashing.

This figure may be reduced if the plant cannot provide extra capacity for the potential increase in base resin production (see section 5.7.4).

5.7.4 The Base Resin Required to Provide the Increase in Potential from Microwave Solids and Ash

For each polyester (requiring base resin) the base resin content was determined (as a % of the initial charge) and the potential calculated as a percentage of the increased production capable from microwave solids and ash.

But, could the plant cope with such an increase?

Assuming that 2 hours (testing time) is saved for each batch of base resin and that one batch takes 24 hours to manufacture, then each reactor saves 14 hours a week (processing time). Therefore, each reactor would be capable of manufacturing one extra batch of base resin every other week, ie 24 additional batches per reactor per working year.

Calculations[9] have shown that such an increase should supply the base resin potential. However, other potential resin production may be lost unless further improvements additional to those from the microwave were implemented.
The loss in potential is equivalent to £54,064.

5.7.5 Increase in Annual Contribution

$$\text{Increased Annual Contribution from Microwave Analysis} = \text{Contribution from Microwave Solids} + \text{Contribution - from Microwave Ash} - \text{Lost Potential}$$

= £477,177 + £361,983 - £54,064
= **£785,096**.

NB - This value must not be taken as an exact figure since there are many external factors, not considered in this report, which will influence this value, eg the assumptions made in section 5.7.1.

5.7.6 Conclusions

1 The increase in annual contribution from microwave solids and ash is potentially £785,096.

2 The increased potential for base resin is achievable through the use of microwave testing for solids.

3 Particular resins cannot be produced at the increased potential rate unless the plant can be further optimised.

5.7.7 Scenario II

After the completion of the preceding calculations, the same BIP source of processing operations altered the basis of procedures from: not charging the reactors while the associated blender was active, to; a proportion of batches (60% on average) were charged while the blender is in operation. This change reduces the extent of possible savings in processing time.

However, this is not strictly true for all resins:

eg (1) Two-stage resins - the second stage is not processed if the reactor's blender is full.

eg (2) Some resins are not processed if the reactor's blender is full and awaiting transfer to a reprocessing blender, ie this may occur if there has been a problem during the production of the reprocessed resin.

Since microwave solids testing does not affect the production of as many resins, the increase in contribution of £477,177 will be reduced.

The resins that will benefit from microwave solids account for approximately 40% of the total plant production.

About one hundred batches of resin are manufactured per month.

∴ 40 batches will benefit from microwave solids.

Assuming that two hours processing time is saved for each of these batches, the plant potentially has an extra 80 hours per month available to increase production, ie 960 hours per annum.

Assuming that on average one batch of resin takes 24 hours to process, then an extra

$$\frac{960}{24} = 40 \text{ batches per annum}$$

could be potentially manufactured.

The production is shared between the reactors: eg between March 1989 and April 1990, 209 batches were manufactured on the smaller reactors and 183 batches on the larger reactors.

Therefore, the potential 40-batch increase in production can be proportionally allocated to the reactors.

Smaller reactors = 21.3 batches
Larger reactors = 18.7 batches.

This is equivalent to:

Smaller reactors = 21.3 x 10 = 213 tonnes
Larger reactors = 18.7 x 20 = 374 tonnes

a potential annual increase in production of 587 tonnes.

Therefore, microwave solids will provide a potential increase in contribution of:

= **£ 290,565.**

Section 5.7.4 indicates that the plant will be able to provide the extra base resin for the potential increase in production possible from microwave solids and ash testing.

∴ Total increase in contribution from microwave analysis:

= contribution from solids + contribution from ash

= £290,565 + £361,983

= **£ 652,548**.

5.8 References

7 Cartlidge, P; "Teaching Company Progress Report for the period March 1989 to May 1989.

8 Cartlidge, P; "Appendix B - Teaching Company Progress Report for the period 24 May 1989 to 8 November 1989.

9 Cartlidge, P; "A Discussion of the Financial Advantages Associated with Microwave Ash and Solids", May 1990.

APPENDICES TO SECTION 1

CHAPTERS 1 - 5

APPENDIX 1

*	***Throughout this Appendix, the terms "oven" solids and "traditional " solids have been used for the same purpose.***

TABLE: 1

Resin Type: AY **Specification: 60 ± 2%**

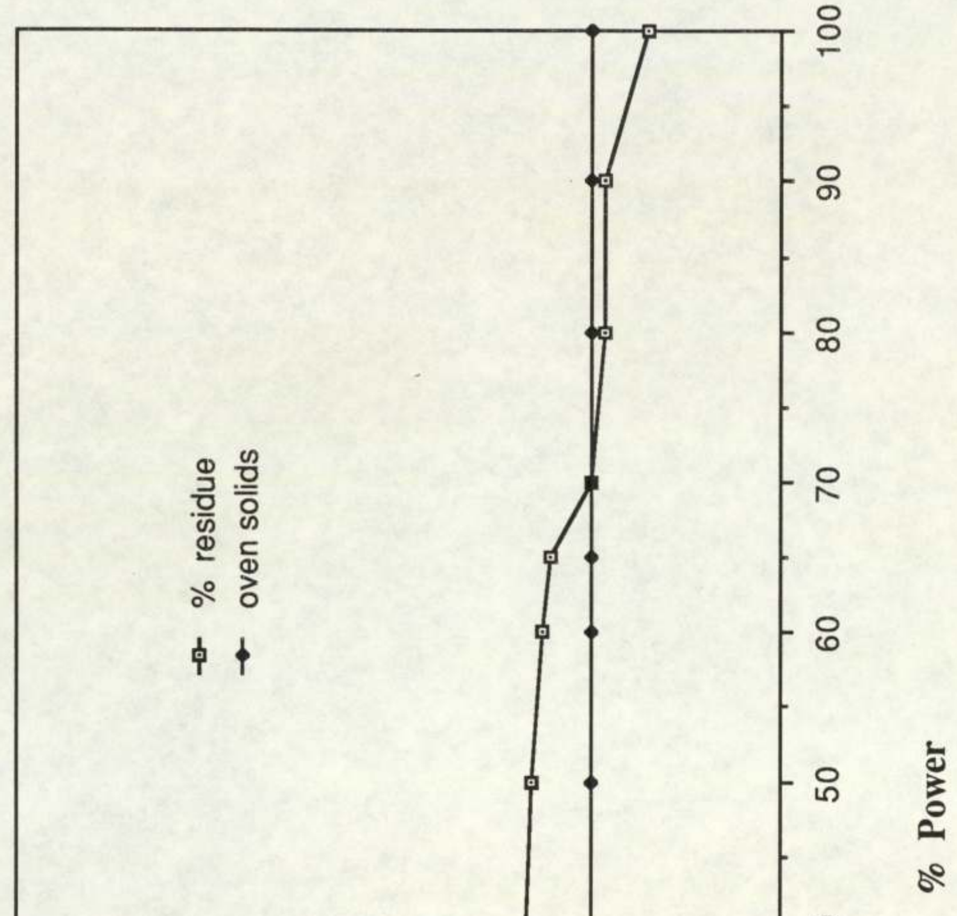
Microwave Conditions:

P1	**100%**	***T1***	**5 minutes**
P2	**68%**	***T2***	**5 minutes**

Batch No	Microwave Solids (%)		Traditional Solids (%)
	x	$\bar{x}$	
442	59.61 60.16 59.89 59.63 60.08 60.51	59.89	60.0
441	60.78 61.30 60.51	60.86	59.6 60.54 (repeat)
440	59.48 60.56 60.68 59.86	60.15	60.4
468	62.2 62.0	62.1	61.6

APPENDIX 1

Figure 1: Microwave Solids, Resin AY/442



APPENDIX 1

TABLE: 2

Resin Type: AM **Specification:** 70 ± 2%

Microwave Conditions:

P1	**100%**	***T1***	**5 minutes**
P2	**52%**	***T2***	**5 minutes**

Batch No	Microwave Solids (%) x	$\bar{x}$	Oven Solids (%)
407	70.89 70.38 70.58 70.04 69.95 70.18	70.34	70.4
408	71.41 69.63 70.68 70.85	70.64	69.8 70.67 (repeat)
409	69.96 70.64 70.46 70.64	70.43	70.0

APPENDIX 1

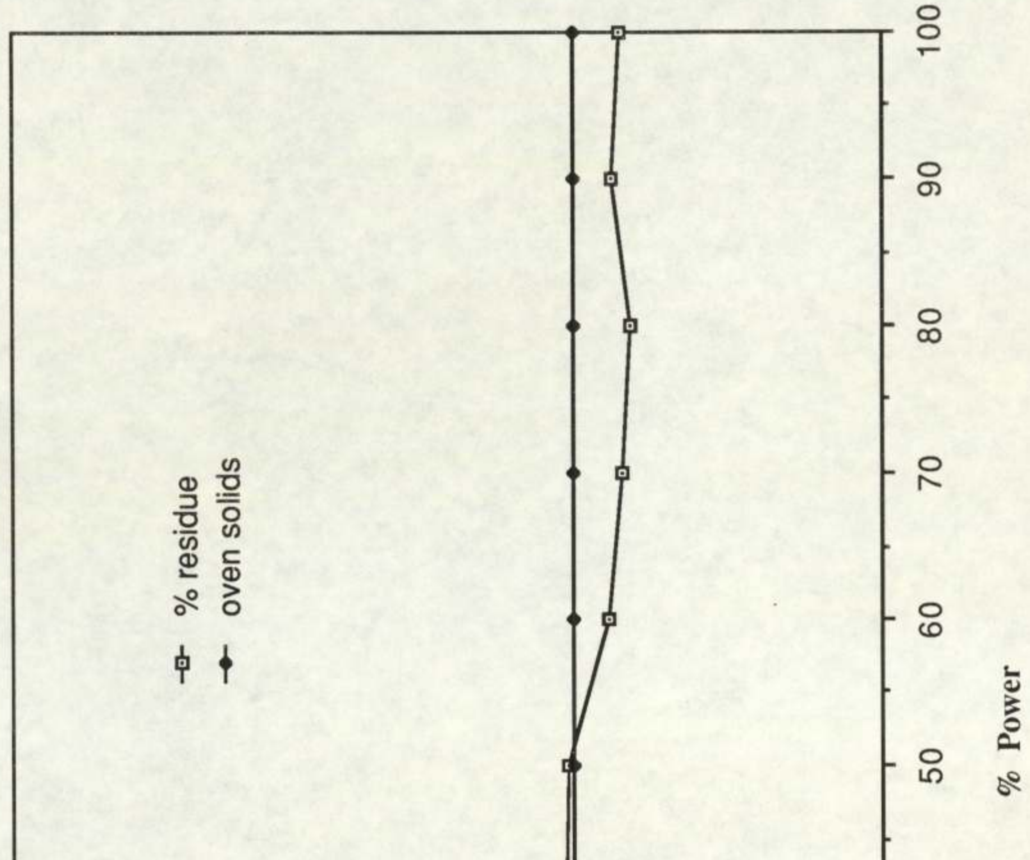


Figure 2: Microwave Solids, Resin AM/408

APPENDIX 1

TABLE: 3

Resin Type: Q **Specification:** **55 ± 2%**

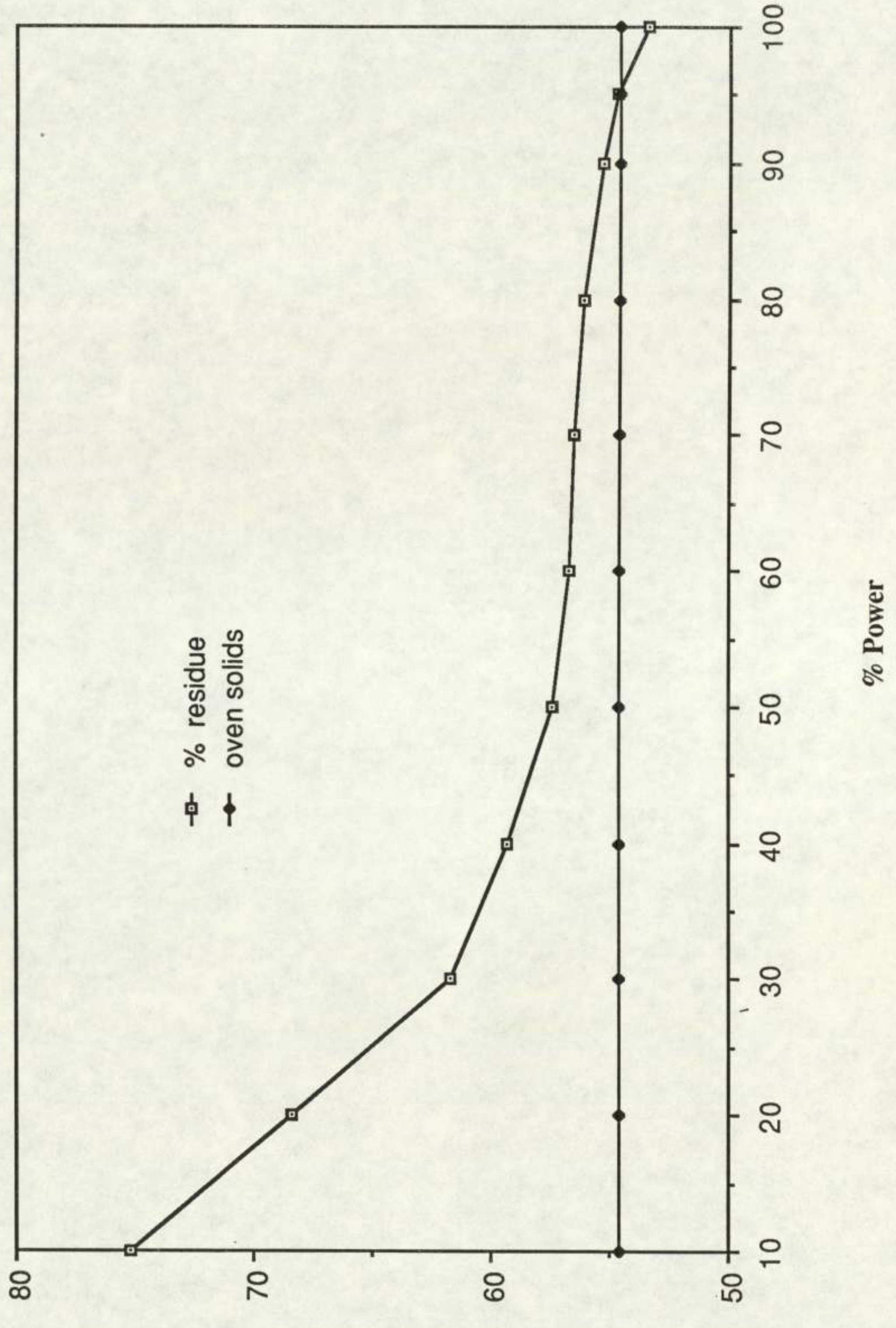
Microwave Conditions:

P1 **100%** ***T1*** **5 minutes**
P2 **98%** ***T2*** **5 minutes**

Batch No	Microwave Solids (%)		Oven Solids (%)
	x	$\bar{x}$	
524	55.5 55.0 54.4 55.5 55.6 55.4	55.2	54.6 55.7 (repeat)
523	55.5 55.3	55.4	54.5 55.7 (repeat)
522	55.9 55.9	55.9	55.0 56.1 (repeat)

APPENDIX 1

Figure 3: Microwave Solids, Resin Q/524



APPENDIX 1

TABLE: 4

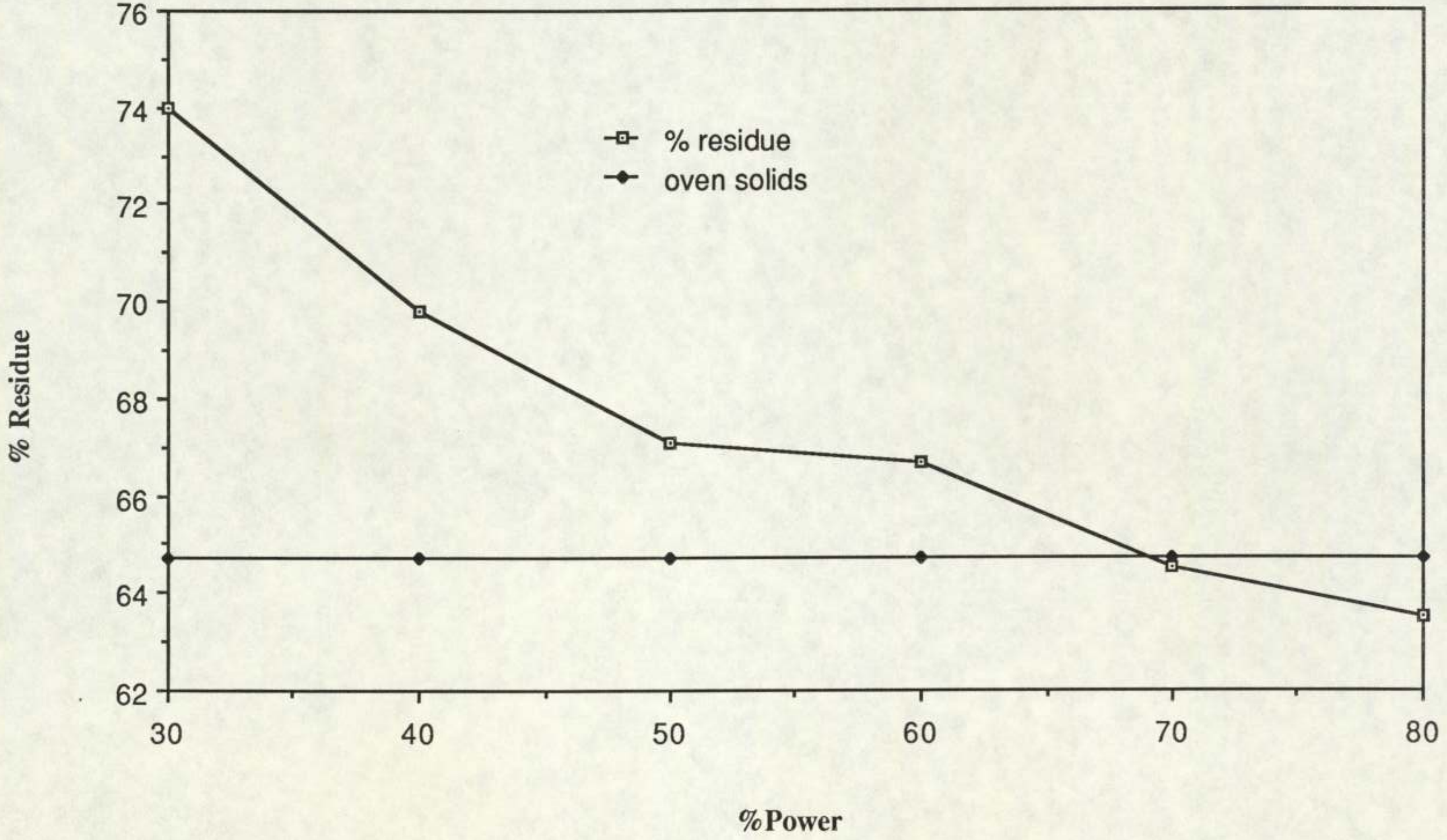
Resin Type: AB **Specification: 65.5 ± 2%**

Microwave Conditions:

P1	**100%**	***T1***	**5 minutes**
P2	**67%**	***T2***	**5 minutes**

Batch No	Microwave Solids (%)		Oven Solids
	x	$\bar{x}$	(%)
939	65.5 65.6 65.7	65.6	65.5
940	65.8 65.2 65.7	65.6	65.9
941	65.5 65.1	65.3	64.7

Figure 4: Microwave Solids, Resin AB/941



APPENDIX 1

TABLE: 5

Resin Type: B **Specification:** **66 ± 2%**

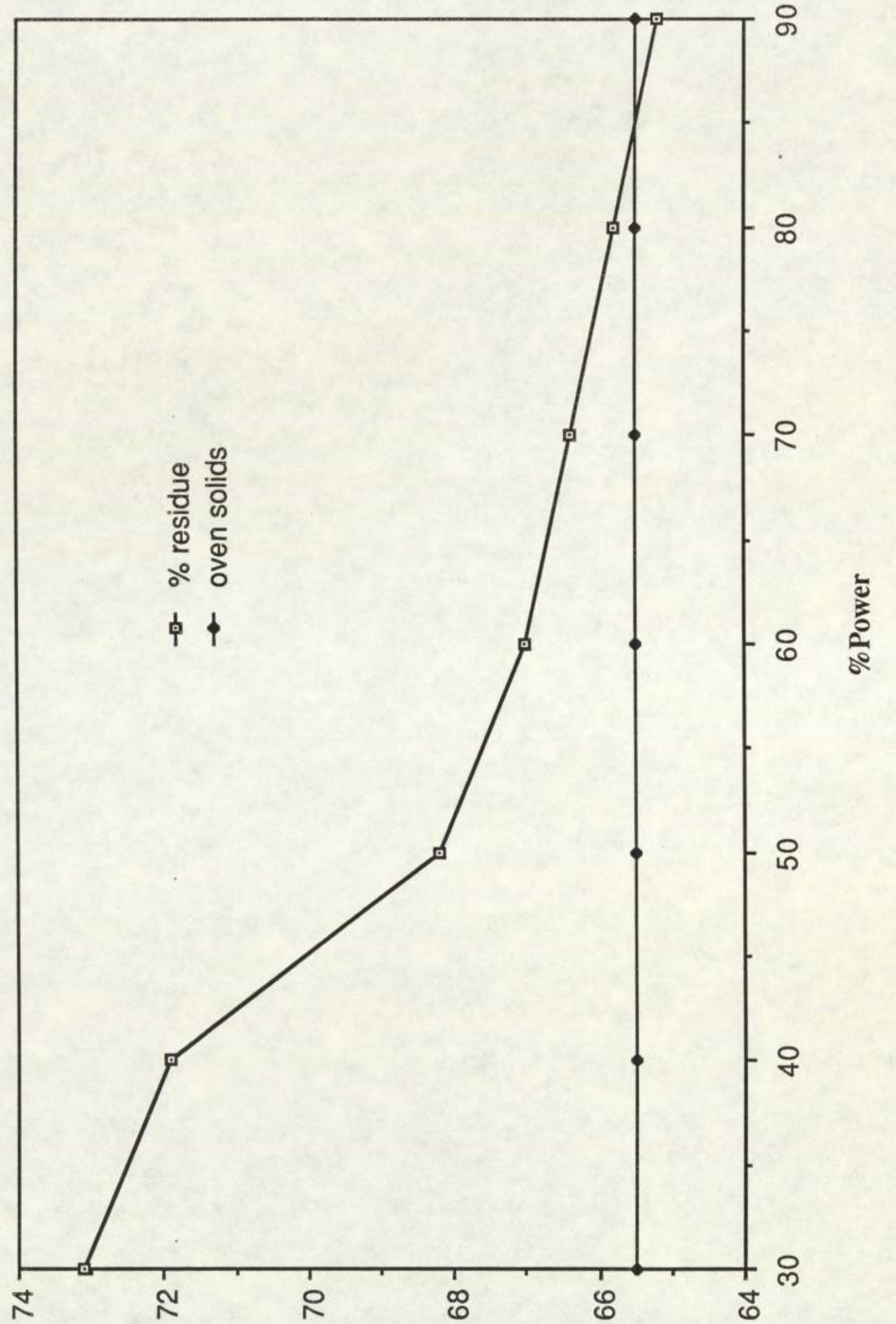
Microwave Conditions:

P1 **100%** ***T1*** **5 minutes**
P2 **80%** ***T2*** **5 minutes**

Batch No	Microwave Solids (%)		Oven Solids (%)
	x	$\bar{x}$	
229	66.0		
	65.9	66.1	66.9
	66.3		
230	66.1		
	65.3	65.7	65.8
	65.6		
231	65.7		
	65.5	65.8	65.5
66.2			

APPENDIX 1

Figure 5: Microwave Solids, Resin B/231



APPENDIX 1

TABLE: 6

Resin Type: AG **Specification:** **70 ± 2%**

Microwave Conditions:

P1 **100%** ***T1*** **5 minutes**
P2 **65%** ***T2*** **5 minutes**

Batch No	Microwave Solids (%)		Oven Solids (%)
	x	$\bar{x}$	
186	71.0 71.1	71.1	71.0
187	70.5 71.1	70.8	70.9
188	70.8 71.6 71.3 70.8	71.1	70.7
241	69.4 69.0	69.2	70.2
242	69.0 70.0	69.5	70.1

APPENDIX 1

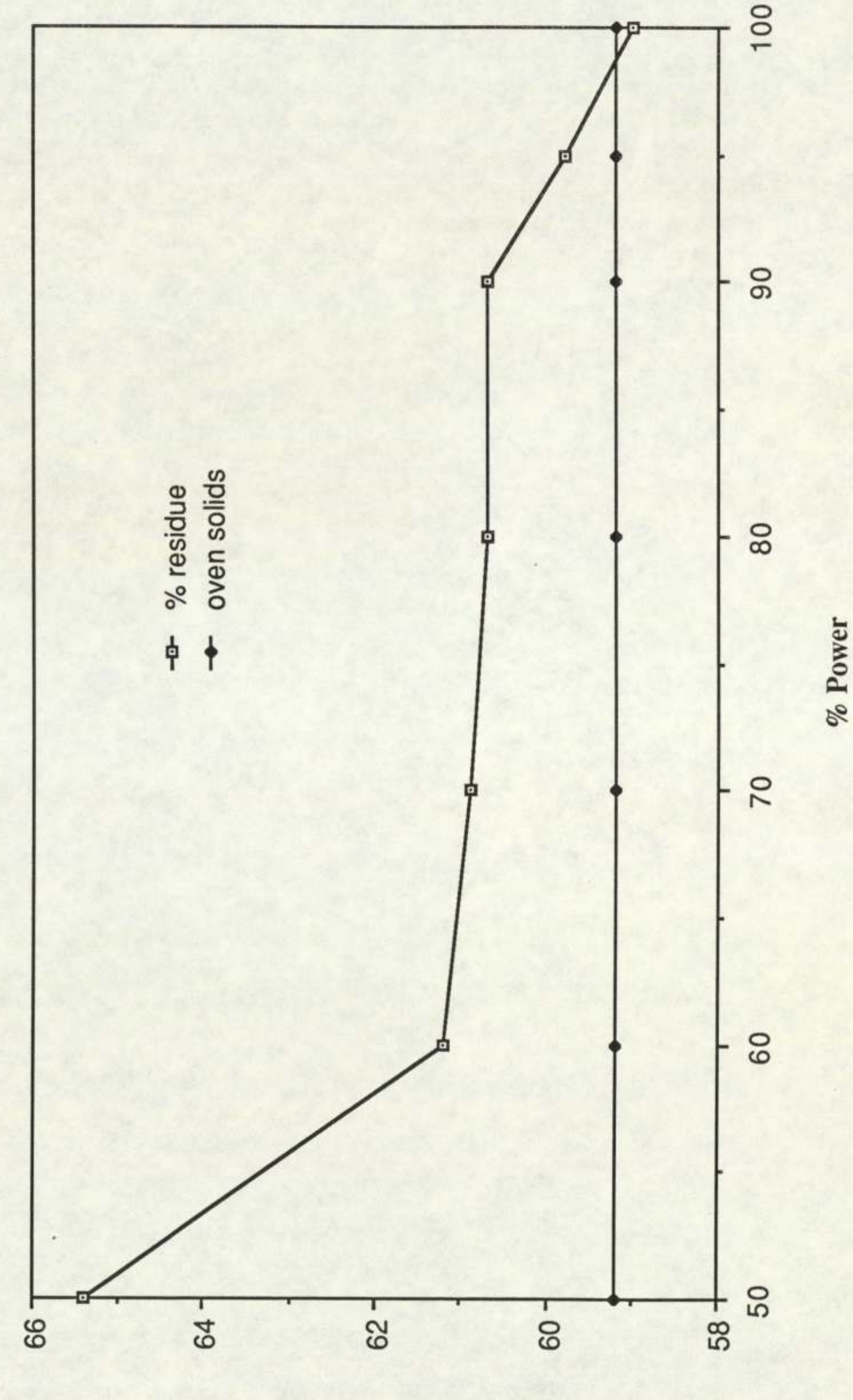


Figure 6: Microwave Solids, Resin W/155

APPENDIX 1

TABLE: 7

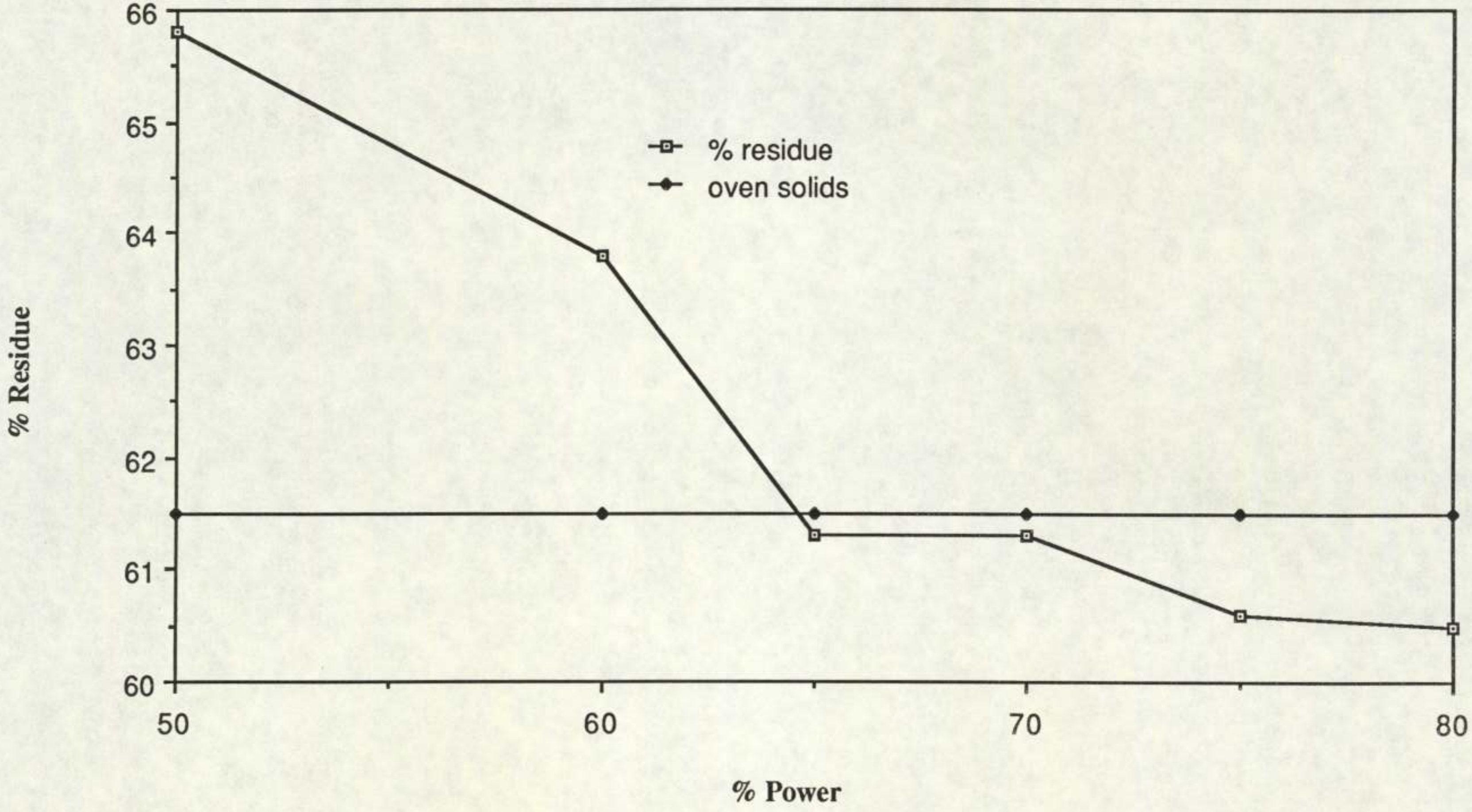
Resin Type: AH **Specification: 73 ± 2%**

Microwave Conditions:

P1	**100%**	***T1***	**5 minutes**
P2	**60%**	***T2***	**5 minutes**

Batch No	Microwave Solids (%)		Oven Solids (%)
	x	$\bar{x}$	
889	73.9 73.8 73.9	73.9	73.2
879	74.0 75.0 75.0 74.1 74.7 74.1	74.5	73.9 75.2 (repeat)
880	74.4 74.3 75.2	74.6	72.8 74.6 (repeat)
915	73.1 73.5	73.3	73.4
920	73.4 72.8	73.1	73.2

Figure 7: Microwave Solids, Resin D/74



APPENDIX 1

TABLE: 8

Resin Type: W **Specification:** **58.5 ± 2%**

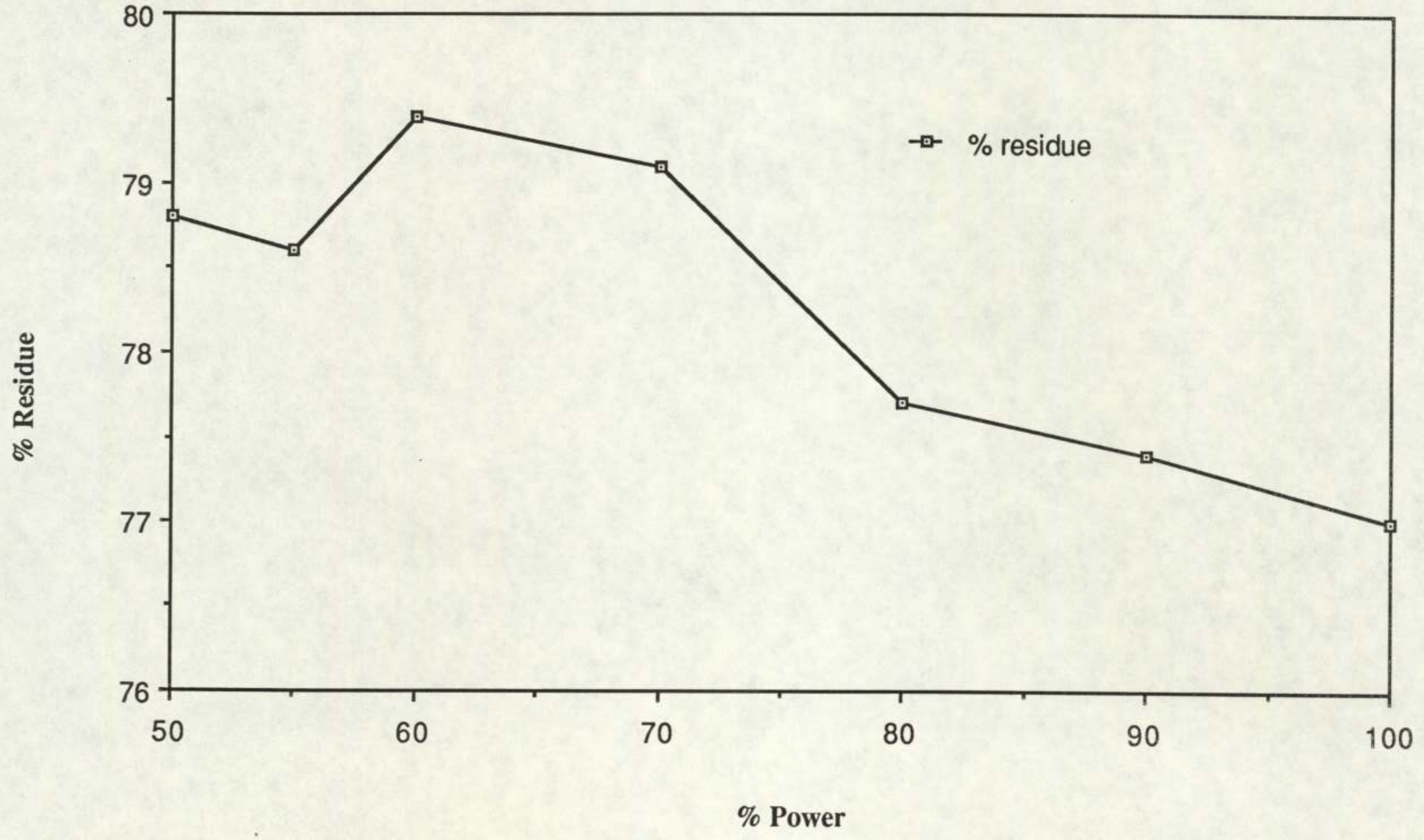
Microwave Conditions:

P1 **100%** ***T1*** **5 minutes**
P2 **95%** ***T2*** **5 minutes**

Batch No	Microwave Solids (%)		Oven Solids
	x	$\bar{x}$	(%)
155	59.6 59.2	59.4	59.2
154	58.1 57.8	58.0	58.4
153	60.0 60.0	60.0	59.5

APPENDIX 1

Figure 8: Microwave Solids, Resin A



APPENDIX 1

TABLE: 9

Resin Type: D **Specification:** **61.5 ± 1.5%**

Microwave Conditions:

P1 **100%** ***T1*** **5 minutes**
P2 **65%** ***T2*** **5 minutes**

Batch No	Microwave Solids (%)		Oven Solids (%)
	x	$\bar{x}$	
71	62.6 62.5	62.6	62.6
73 61.5	61.3	61.4	61.4
74	60.5 61.3 61.2 60.7	60.9	61.4

APPENDIX 1

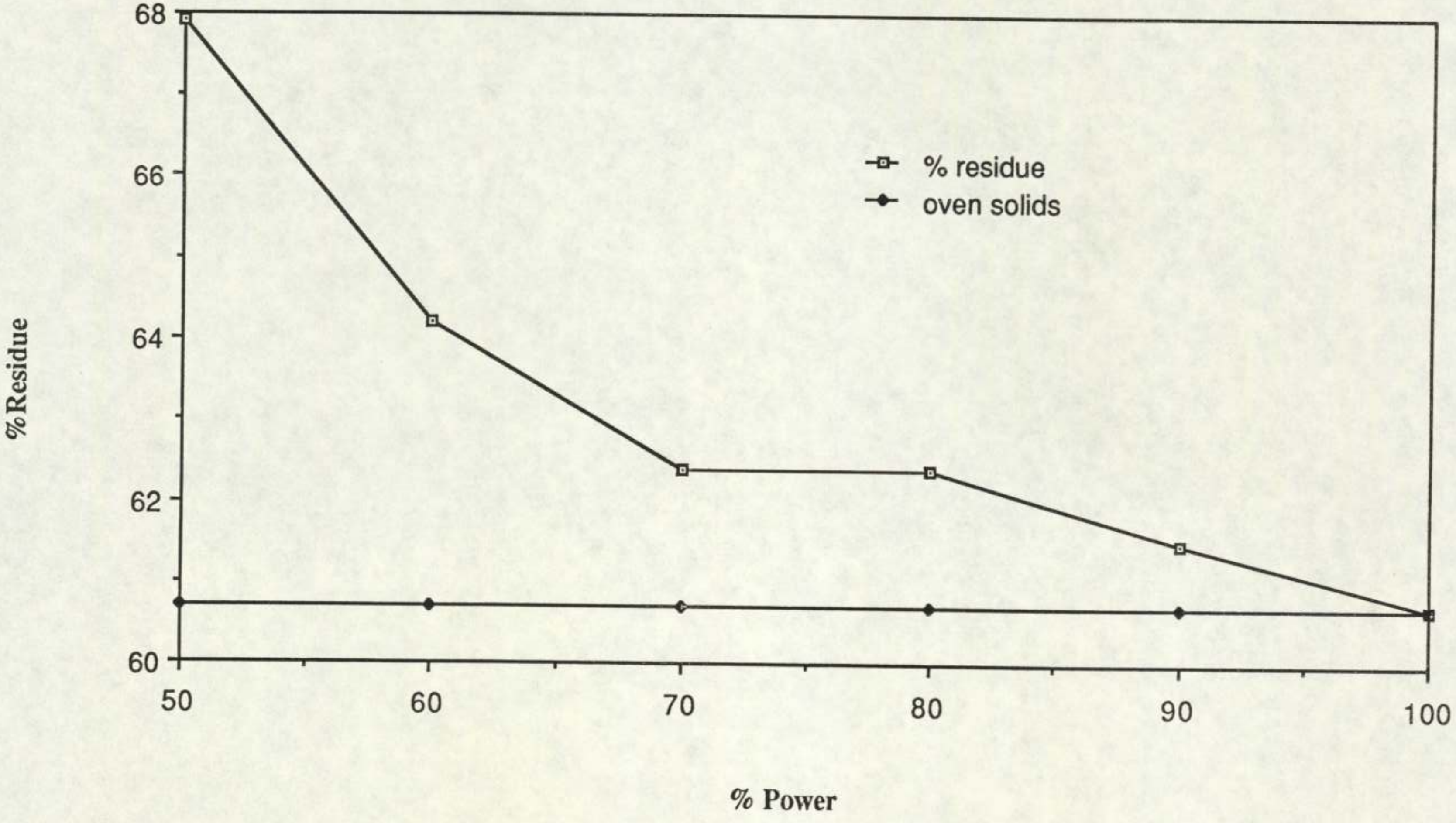


Figure 9: Microwave Solids, Resin Z/200

APPENDIX 1

TABLE: 10

Resin Type: R **Specification:** **55± 2%**

Microwave Conditions:

P1 **100%** ***T1*** **5 minutes**
P2 **98%** ***T2*** **5 minutes**

Batch No	Microwave Solids (%)		Oven Solids (%)
	x	$\bar{x}$	
120	55.0	55.0 54.9	55.2
121	53.8 53.0 53.6	53.5	54.4
122	57.1 56.9	57.0	55.2 55.7 (repeat)
123	54.0 53.4	53.7	54.5
124	53.7 53.7	53.7	54.7 54.9 (repeat)

APPENDIX 1

TABLE: 11

Resin Type: A **Specification:** **75 ± 2%**

Microwave Conditions:

P1 **100%** ***T1*** **5 minutes**
P2 **100%** ***T2*** **5 minutes**

Batch No	Microwave Solids (%)		Oven Solids (%)
	x	$\bar{x}$	
142	77.0 77.7 78.0 77.0	77.4	76.0 76.6 (repeat)
141	77.3 76.7	77.0	76.0 75.2 (repeat)
140	76.8 76.7	76.8	76.0 75.6 (repeat)

APPENDIX 1

TABLE: 12

Resin Type: BH **Specification:** **56 ± 2%**

Microwave Conditions:

P1	**100%**	***T1***	**5 minutes**
P2	**100%**	***T2***	**10 minutes**

Batch No	Microwave Solids (%)		Oven Solids (%)
	x	$\bar{x}$	
37	56.0		
	55.7	55.9	55.4
	55.9		
36	57.0		
	57.6	60.86	55.9
58.8			
	55.2		
35	55.6		
	55.5	55.8	55.9
	56.4		

APPENDIX 1

TABLE: 13

Resin Type: Z **Specification: 61 ± 2%**

Microwave Conditions:

P1 **100%** ***T1*** **5 minutes**
P2 **100%** ***T2*** **5 minutes**

Batch No	Microwave Solids (%)		Oven Solids (%)
	x	$\bar{x}$	
200	60.7 60.3 60.3	60.4	60.7
199	60.9 60.5	60.7	60.0
198	61.0 62.0	61.5	62.0

APPENDIX 1

TABLE: 14

Resin Type: AX **Specification: 62 ± 1.5%**

Microwave Conditions:

P1 **100%** ***T1*** **5 minutes**
P2 **75%** ***T2*** **5 minutes**

Batch No	Microwave Solids (%)		Oven Solids (%)
	x	$\bar{x}$	
643	62.7 62.5 62.5	62.6	62.2
642	62.5 63.2 62.6	62.8	62.6
641	62.7 62.9 62.0	62.5	62.7

APPENDIX 1

TABLE: 15

Resin Type: AK **Specification:** **66.5± 2%**

Microwave Conditions:

P1	**100%**	***T1***	**5 minutes**
P2	**70%**	***T2***	**5 minutes**

Batch No	Microwave Solids (%)		Oven Solids (%)
	x	$\bar{x}$	
90	66.7 66.5 66.4	66.5	66.4
89	66.0 66.2 66.4	66.2	66.1
88	66.5 66.7	66.6	66.5

APPENDIX 1

TABLE: 16

Resin Type: BF **Specification:** **65.5 ± 2%**

Microwave Conditions:

P1	**100%**	***T1***	**5 minutes**
P2	**70%**	***T2***	**5 minutes**

Batch No	Microwave Solids (%)		Oven Solids (%)
	x	$\bar{x}$	
148	67.4 66.9 67.6	67.3	66.8
147	66.3 66.4	66.4	65.9
146	66.2 66.5	66.4	66.4

APPENDIX 1

TABLE 17

OVEN SOLIDS

RESIN = AY **OVEN SOLIDS % = 61.2**

BATCH NUMBER = 318

Sample	Oven Solids %		
	(i)	(ii)	(x)
1	60.59	60.53	60.56
2	60.31	60.55	60.43
3	61.01	61.14	61.08
4	60.77	60.85	60.81
5	61.17	60.49	60.83
6	61.88	60.90	61.39
7	61.37	61.36	61.36
8	61.53	61.28	61.41
9	60.83	61.45	61.14
10	60.94	60.77	60.86

Standard Deviation of all the results:-

$x = 60.99$

$\sigma_n = 0.397$

$\sigma_{n-1} = 0.407$

APPENDIX 1a

RESINS QUALITY CONTROL		**Method No:**	2/SRY-8A
TEST METHOD FOR:		**Issue No**	2
		Issue Date:	14.5.90
SOLID RESIN YIELD - MICROWAVE		**Page No:**	1 of 5

APPARATUS

Microwave MDS-81 with Turntable
2 Thermapads (120°C)
Glass Fibre Sample Pads
Analytical Balance accurate to 1mg

METHOD

1 Ensure that the inside of the microwave is clean. Clean thermapads at beginning of each shift.

2 Follow the attached set up procedure to establish microwave conditions.

3 After setting up the microwave press the **START** button to warm up the thermapads before analysis.

4 Accurately weigh out a duplicate sample while the thermapads are warming up (ie during the 5-minute pre-run - refer to set up procedure).

NB

If the machine has just been switched on; the pre-run time is 10 minutes.

For each sample:-

(i) Weigh out three sample pads (W1).

(ii) Weigh 2g ± 0.005g of resin onto the pads and spread evenly over the surface. Re-weigh pads (W2).

(iii) Remove the lower pad and place it on top of the sample to form a 'sandwich'.

5 At the end of the pre-run, place the samples onto the thermapads.

6 When the sample run is finished, remove the sample pads from the microwave and re-weigh (W3).

CALCULATION

$$\text{Solid Resin Yield} = \frac{W3 - W1}{W2 - W1} \times 100\%$$

The result is to be reported as the mean of the two determinations provided that the two determinations do not differ by more than one unit (ie 1%).

RESINS QUALITY CONTROL

Prepared By:

Authorised by:

APPENDIX 1a

RESINS QUALITY CONTROL	**Method No:**	2/SRY-8A
TEST METHOD FOR:	**Issue No**	2
	Issue Date:	14.5.90
SOLID RESIN YIELD - MICROWAVE	**Page No:**	3 of 5

SETTING UP THE MICROWAVE FOR THE DETERMINATION OF SOLID RESIN YIELD

1 Place the turntable and thermapads into the microwave. (The thermapads should be placed directly opposite each other on the turntable.)

2 Set up the microwave as follows:-

	Action	Display
(i)	Switch on the microwave	S1 P = % T =
	Establish a pre-run to warm up the thermapads	
(ii)	Set T at 5.00 mins using the numeric keys.	
(iii)	Press **ENTER**	S1 P = % T = 5.00
(iv)	Set P at 100% using the numeric keys	
(v)	Press **ENTER**	S1 P = 100% T = 5.00
	Establish conditions for sample analysis	
(vi)	Press **PROGRAM**	S2 P = % T =
(vii)	**REFER TO TABLE 1 FOR INDIVIDUAL RESIN CONDITIONS**	
(viii)	Enter the appropriate power and time by following actions (ii) to (v)	S2 P = x % T = x
(ix)	Press **RESET**	S1 P = 100% T = 5.00

NOTE

The exhaust fan is to be set in the medium position (before analysis).

APPENDIX 1a

RESINS QUALITY CONTROL
TEST METHOD FOR:

SOLID RESIN YIELD - MICROWAVE

Method No:	2/SRY-8A
Issue No	2
Issue Date:	14.5.90
Page No:	4 of 5

TABLE 1 MICROWAVE CONDITIONS FOR THE DETERMINATION OF SOLID RESIN YIELD

Resin	Run Time (mins)	Power (%)
A	15	100
B	5	80
C	5	83
D	5	70
E	12	100
F	12	100
G	10	100
H	15	100
I	5	50
J	10	100
K	10	100
L	5	100
M	5	95 (Provisional)
N	10	100
O	10	98
P	5	100
Q	10	100
R	10	100
S	7	100
T	12	100 (Provisional)
U	10	100
V	5	100
W	5	100
X	7	100
Y	10	100 (Provisional)
Z	5	100
AA	5	80 (Provisional)
AB	5	80
AC	5	80
AD	5	60
AE	10	1005 AF 5
100		
AG	5	70
AH	5	65
AI	5	90

RESINS QUALITY CONTROL TEST METHOD FOR:	**Method No:**	2/SRY-8A
	Issue No	2
	Issue Date:	14.5.90
SOLID RESIN YIELD - MICROWAVE	**Page No:**	5 of 5

Resin	**Run Time (mins)**	**Power (%)**
AJ	5	80
AK	5	70
AL	10	100
AM	5	65
AN	10	85
AO	5	65
AP	5	100
AQ	5	75
AR	20	100
AS	7	100
AT	10	100
AU	10	100
AV	5	100
AW	15	100
AX	5	85
AY	5	95
AZ	5	95
BA	10	100 (Provisional)
BB	7	100 (Provisional)
BC	5	80
BD	15	100 (Provisional)
BE	5	70
BF	5	90
BG	5	100 (Provisional)
BH	10	100
BI	5	100

NOTE

PROVISIONAL indicates that the conditions have been established using one or two batches. More work will be required to confirm these conditions.

APPENDIX 1b

TABLE: 1

Resin Type: AH **Specification:** **13.0% - 14.3%**

Batch No	Microwave Ash (%)			Oven Ash (%)
	(i)	(ii)	$\bar{x}$	
844	13.93	13.74	13.84	14.0
844	14.08	-	14.08	14.0
845	13.69	13.43	13.56	13.6
846	13.98	14.05	14.02	14.0
846	14.05	-	14.05	14.0
850	13.71	13.63	13.67	13.9
850 (F10)	13.93	-	13.93	14.3
856	13.89	13.97	13.93	14.0
857 (FI0)	13.70	13.64	13.67	13.7
859 (FI0)	13.61	13.72	13.67	14.0
861 (FI0)	13.68	13.63	13.66	13.6

APPENDIX 1b

TABLE: 2

Resin Type: AG **Specification:** **2.0% - 3.0%**

Batch No	Microwave Ash (%)			Oven Ash (%)
	(i)	(ii)	$\bar{x}$	
117	2.38	2.56	2.47	2.60
117 (FIO)	2.66	2.76	2.71	2.00
118	2.64	2.54	2.59	2.39
137	2.42	-	2.42	2.50
70	2.42	-	2.42	2.48

TABLE: 3

Resin Type: A **Specification: 26.5% - 29.5%**

Batch No	Microwave Ash (%)			Oven Ash
	(i)	(ii)	$\bar{x}$	(%)
134	26.86	-	26.86	27.2
135	26.78	27.03	26.90	26.7
136	28.61	28.42	28.51	28.7
137	26.61	26.80	26.70	26.8
138	26.66	26.71	26.68	26.97
139	26.40	26.58	26.49	26.3 (fail)
139	26.50	-	26.50	26.3 (fail)

APPENDIX 1b

TABLE: 4

Resin Type: AW **Specification: 18.5% - 21.5%**

Batch No	Microwave Ash (%)			Oven Ash (%)
	(i)	(ii)	$\bar{x}$	
267	19.90	19.92	19.91	20.02
268	18.97	18.98	18.98	19.2
269	19.94	-	19.94	20.0
270	20.99	20.98	20.99	20.9
271	21.16	-	21.16	21.14
272	20.14	20.24	20.19	20.3

TABLE: 5

Resin Type: AJ **Specification: 1.5% - 2.1%**

Batch No	Microwave Ash (%)			Oven Ash
	(i)	(ii)	$\bar{x}$	(%)
183	1.86	1.98	1.92	1.90
184	1.72	1.68	1.70	2.00
185	1.82	-	1.82*	1.51
186	1.74	1.70	1.72	1.64
187	1.94	1.70	1.82	1.66
188	1.88	1.76	1.82	1.88
189	1.62	1.60	1.61	1.70
190	1.41	1.50	1.46	1.59
190	1.56	-	1.56	1.59

* Result after 30 minutes = 1.78%

TABLE: 6

Resin Type: AK **Specification: 13.0% - 14.0%**

Batch No	Microwave Ash (%) (i)	(ii)	$\bar{x}$	Oven Ash (%)
81	13.58	13.58	13.58	13.6
82	13.56	13.57	13.57	13.8
83	13.57	13.77	13.67	13.7
84	13.78	-	13.78	13.6
85	13.42	-	13.42	13.5
86	13.34	13.20	13.29	13.5
88	13.51	13.42	13.47	13.4
88	13.48	-	13.48	13.4

TABLE: 7

COMPARATIVE ANALYSIS OF DIFFERENT RESIN TYPES

Resin Type/Batch No	Microwave Ash (%)	Oven Ash (%)
AG/70	2.70	2.48
AH/838	14.11	13.70 (FIO 14.0%)
AG/70	2.48	2.48
A/138	26.55	26.97
AW/271	21.19	21.14
A/138	26.61	26.97
AG/101	2.42	2.53
AH/847	14.01	14.17
AG/102	2.50	2.30
AH/848	14.02	14.10
AG/103	2.55	2.48
AH/849	14.01	14.27

APPENDIX 1c

RESINS QUALITY CONTROL
TEST METHOD FOR:

ASH CONTENT - MICROWAVE

Method No: 2/A-4
Issue No: 1
Issue Date: 15.3.90
Page No: 1 of 3

APPARATUS

Microwave MDS-81 with Muffle Furnace at 800°C
Quartz Fibre Crucible with 2 Disposable Quartz Fibre Discs
Analytical Balance accurate to 0·1mg

METHOD

1) Ensure that the inside of the microwave is clean, ie., free from any deposits.

2) Follow the attached set up procedure to establish ash conditions.

3) Accurately weigh a clean crucible and 2 disposable discs.

4) Place one of the discs in the crucible (to provide a base) and then weigh 5g ± 5mg of sample into the crucible. The second disc is then gently placed onto the sample to provide a lid.

5) The sample can then be ashed by placing the crucible into the muffle at 800°C for the required length of time :-

    (i) one sample for 20 minutes

    (ii) two samples for 25 minutes.

6) Remove the crucible from the muffle and re-weigh the crucible, 2 disposable discs and residue.

CALCULATION

$$\% \text{ Ash w/w} = \frac{100 \times R}{W}$$

where:

R = weight of residue (g)
W = weight of sample (g)

RESINS QUALITY CONTROL

Prepared By:

Authorised By: J. D. Newell

SET UP PROCEDURE FOR ASHING, USING THE MICROWAVE MDS-81

1) Place the ashing block and temperature probe into the microwave.

2) Set up the temperature controller as follows :-

Action	Display
	- Shows temperature of probe
(i) Press S	
	- Set up O
(ii) Enter 28 using ↑ & ↓ keys	
	- 28
(iii) Press S	
	- °C or °F - °C
(iv) Press S	
	- SP1H
(v) Set ashing temp. of 800°C using ↑ & ↓ keys	
	- 800
(vi) Press S	
	- SP1L - O
(vii) Press S	
	- SP2H - 2499
(viii) Press S	
	- SP2L - O
(ix) Press S	
	- HYS - 1
(x) Press S	
	- Run - Temperature of probe

3) Heat the muffle furnace to 800°C by running the microwave on 100% power for the required length of time. (Note: If heating the furnace from room temperature, then allow at least 30 minutes to reach 800°C).

4) Enter the required run time (See Test Method).

After programming the time, press the ENTER button so as to record the conditions in the memory of the microwave.

5) The microwave is now ready to run. Samples can be analysed by pressing the START button.

<u>NOTE:</u> **ALL SAMPLES ARE ASHED ON 100% POWER**

SECTION 2

CHAPTER 6

OPTIMISATION OF REACTOR 5

6 OPTIMISATION OF REACTOR 5

The operation of the reactor 5 (R5) partial condenser, commissioned by the Teaching Company Scheme[9], was evaluated to optimise its performance and permit resin manufacture via the modified fusion process (see chapter 3). At approximately the same time, a mass flowmeter was installed into the distillate line of this reactor. The meter will monitor glycol losses from the reactor (by measuring the composition of distillate) and the rate of removal of distillate. This will provide a better understanding of the course of reaction and hopefully result in better control of the reactor overhead system.

Optimisation of this equipment should improve the productivity of the reactor. The performance of the partial condenser and commissioning of the mass flowmeter will be discussed separately in the major subsections of this chapter.

6.1 Commissioning of the Mass Flowmeter

6.1.1. Introduction

The mass flowmeter was installed in the distillate line of R5 (see figure 6.1) to monitor the distillate from both the separator and the by-pass condenser. This means that all distillate can be passed through the meter whether the solvent, distillate reflux or fusion process is used.

The mass flowmeter is capable of providing a running total of the quantity of distillate leaving the reactor (see section 6.1.2). In addition, the continuous density measurement allows the composition of the distillate to be monitored, provided the distillate is a two-component mixture. Earlier work[10] indicated that for fusion resins the density of the distillate was an accurate measure of composition, giving consistent results when compared with the refractive index of the sample. The accuracy is reduced for solvent process resins, since small quantities of xylol are carried over with the distillate. It is expected that density analysis of fusion process distillate will be accurate to approximately one mass per cent. This may fall to approximately five mass per cent for solvent process batches.

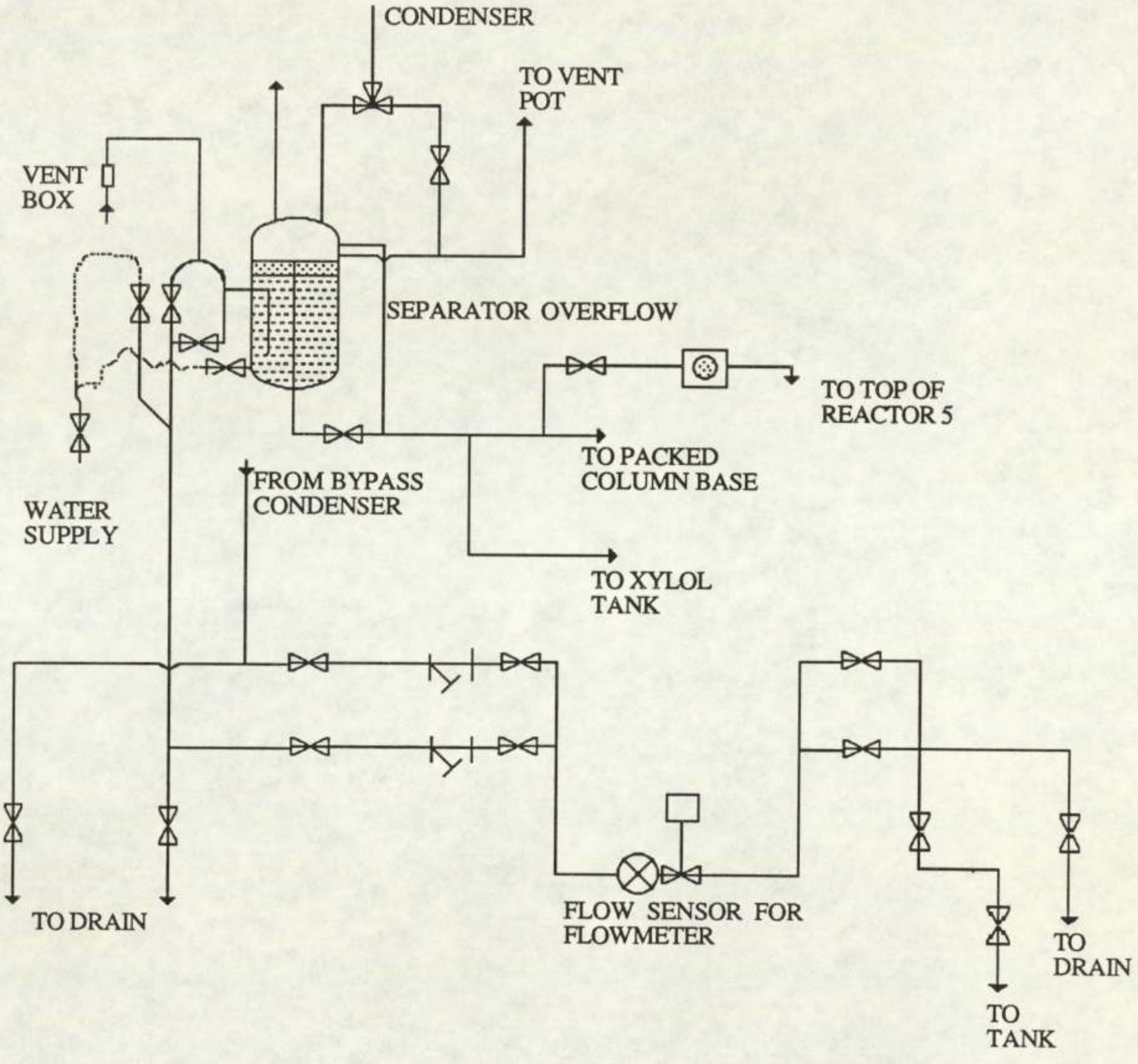


FIGURE 6.1; FLOW DIAGRAM SHOWING POSITION OF MASS FLOWMETER

It is hoped that the mass flowmeter will benefit the plant in two ways:-

(1) Relate the water removed from the reactor to the acid value of the resin.

This will provide an indication of the course of reaction and may ultimately result in the removal of the acid value test if computer control is to be introduced on the polyester plant, ie by interfacing the mass flowmeter, column top temperature and cooling water flow rate of the partial condenser with a Personal Computer.

(2) Accurate assessment of the point at which the by-pass condenser is selected:

It is stated that reaction times of resins produced using the partial condenser were extended (see section 6.2). This may be because the exchanger is too large, allowing more water than is necessary to return to the reactor and also because the by-pass condenser is not always used as soon as it might be, ie in many cases the temperature at the top of the partial condenser falls below 90°C when the acid value of the resin is still quite high. If by-pass is selected too early, unreacted glycol may be lost, resulting in an out of specification resin. The mass flowmeter will enable profiles of the rate of evolution of water to be determined. The point at which the by-pass condenser is used can then be expressed in terms of the total distillate removed from the reactor, and should result in a more consistent operation of the reactor. In addition, a continuous density measurement will provide a double-check on the column top temperature, and by checking the composition of distillate, will provide an indication as to whether the system is losing glycol. It will also provide a cross check on the accuracy of the indicated temperature from vapour-liquid equilibrium data.

6.1.2 The Mass Flowmeter and Principles of Operation

The installed mass flowmeter is an Exac model 8300 version 1.2. Relative to its present application, this highly versatile meter is capable of measuring: mass flow (kg/min), mass total (kg), density (gcc), temperature (°C), real volume total (ltrs) and % solids. The philosophy of the meter is that mass always remains constant and therefore provides a more reliable measurement, ie flow can be measured by either mass or volume. However, mass is more accurate, because mass, unlike volume, is not affected by changes in temperature, pressure, density or viscosity. The mass flowmeter uses the Coriolis effect (see figure 6.2) to measure flow rate directly, ie when acceleration is applied to a rotating mass, it creates gyroscopic forces. The twin loops within the sensor of the mass flowmeter (see figure 6.3) are deflected in proportion to the mass flow rate. This deflection is sensed by electromagnetic detectors and converted to digital signals.

The main specifications of interest were the accuracy of the mass total and density measurements. For density the manufacturer's specifications are:-

-	accuracy:	± 0.01 g/cc
-	repeatability:	± 0.003 g/cc
-	range:	0.3 to 3.0 g/cc.

One of the objectives during commissioning was to reduce the error in the density reading to less than the repeatability and check its consistency. Reducing the instrument error will increase the accuracy of estimation of glycol losses. Other plant equipment/instrumentation was also used to monitor the course of reaction and thus observe the amount of distillate removed with time during reaction, variation in distillate flowrate, variations in the column top temperature and variations in the cooling water flowrate.

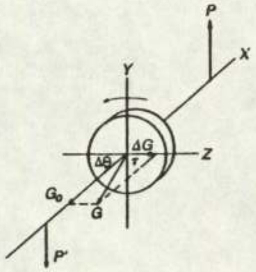
6.1.3 Setting Up the System

Before distillation starts (ie below 150°C) the mass flowmeter is switched on (to warm up the sensor) and the valves re-arranged to allow distillate to flow through the mass flowmeter as opposed to the drain (see figure 6.1). The distillate lines are then cleaned by washing through with water until the density of water is recorded on the meter. (The distillate line can be connected to South Staffordshire water to enable the meter to be cleaned between batches.) When clean, the mass flowmeter is ready to monitor the distillate.

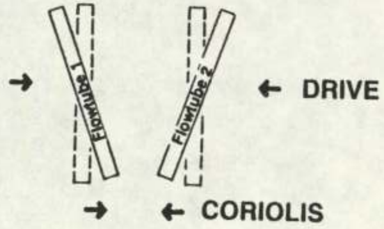
Figure 6.3 shows a schematic diagram of both the sensor and transmitter. The transmitter is housed outside the plant area due to a lack of intrinsic safety.

FIGURE 6.2

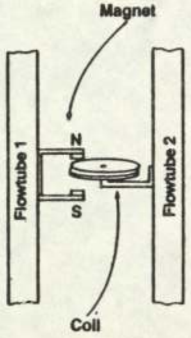
THE CORIOLIS EFFECT



Gyroscopic deflection of the tubes occurs when a fluid flows through the twin loops of the vibrated EXAC flow sensor.



This Coriolis deflection is proportional to the mass flow rate.

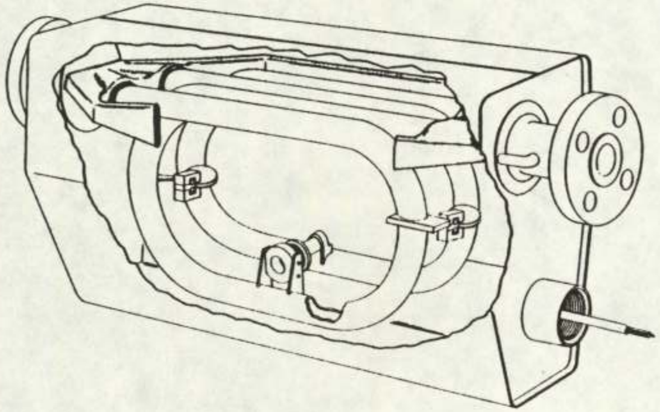


Electromagnetic detectors sense the deflections.

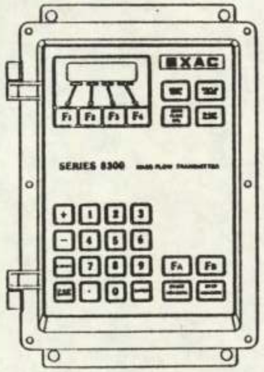
FIGURE 6.3

THE EXAC MASS FLOWMETER

SERIES EX
FLOW SENSOR



SERIES 8300
TRANSMITTER



Wetted components are all 316L stainless steel

Flow rate from 0.12 to 13,500 lb/min

Low pressure drop

Powerful microprocessor

Easy to configure to meet the needs of specific installations

Self diagnostics

The relevant data are obtained from the transmitter by pressing the Display Mode button, followed by the appropriate numerical keys:

eg:	00	to obtain	mass flow (kg/min) density (g/cc)
	01	to obtain	volume flow (ltrs/min) total volume (ltrs)
	02	to obtain	temperature (°C) total mass flow (kg).

6.1.4 Results and Discussion

See Tables 1 - 4 of Appendix 2.

The majority of the results come from runs three and four, resins AX/634 and AY/395, respectively (see Tables 3 and 4 of Appendix 2). The reason for this is that the accuracy of the meter had not been proven for previous runs. The results from run three[11] were checked by collecting distillate samples and measuring the percentage weight propylene glycol by the flowmeter density, refractometry and densitometry, the latter two by means of laboratory analysis. The data from run four (see Table 4) could not be used as they were beyond the scope of the correlation tables with respect to temperature. The data could, however, be used to assess to some degree the propylene glycol loss over the batch.

Table 6.1 summarises the data collected for AX/634. There appears to be no consistent difference in the calculated percentage propylene glycol when comparing the results from the flowmeter with the two laboratory methods. The data from each method has been adjusted to account for temperature effects to give the true percentage weight of glycol. The slight discrepancies between each test method may be attributable to the time delay between taking a density reading and collecting the sample of liquid which was flowing through the flow sensor at that time. Other factors include human error in taking the readings, instrument error in the fourth decimal place and liquid mixing within the tubes of the flow sensor and downstream pipework. Table 6.1 shows the worst deviation to be 3.48 mass % glycol between the

DATE:1/12/89 TABLE 6.1 RESULTS SUMMARY : RUN 3
% WEIGHT PROPYLENE GLYCOL
(AFTER ADJUSTMENTS)

TIME(REAL)	FLOWMETER(F)	REFRACTIVE INDEX(N)	DENSITOMETER(D)	(F)-(N)	(F)-(D)	(N)-(D)
1345	0.44	1.6	0.14	1.16	-0.3	1.46
1445	0.21	2.97	1.11	2.76	0.9	1.86
1535	8.35	11.19	10	2.84	1.65	1.19
1630	14.25	16.92	15.4	2.67	1.15	1.52
1700	14.13	16.11	14.9	1.98	0.77	1.21
1730	12.53	16.01	14.7	3.48	2.17	1.31

FLOWMETER (25 C) : 0.0001g/cc -0.14% PROPYLENE GLYCOL

REFRACTIVE INDEX: (25 C) 0.0001 - .09% PROPYLENE GLYCOL

DENSITOMETER: (25 C) 0.0001g/cc -0.14% PROPYLENE GLYCOL flowmeter and refractive index readings at 17.30. However, this is still within the repeatability error for the flowmeter:

ie $\quad 3.48\% = 0.0023$ g/cc (< 0.003 g/cc - see section 6.1.2).

Which value the actual repeatability takes is hard to quantify without an accurate assessment of the errors inherent in the laboratory equipment. Samples taken closer to the flow sensor may improve knowledge of this value.

The data from runs three and four (see Tables 3 and 4 of Appendix 2) enables assessment of the propylene glycol lost in the distillate (see section 6.1.4.1). The theoretical water of reaction can be calculated (from reactant charges and reactivities) and used to estimate glycol losses for the complete batch. The acid value recorded in run 4 provides an indication of the water removed from reaction at that stage. This figure may be used in conjunction with the glycol lost to indicate the total distillate removed at that stage of reaction and subsequently relate it to the total mass of distillate recorded by the meter (see section 6.1.4.1).

6.1.4.1 Calculation of Glycol Lost in the Distillate

Using :

$$\left[\text{ mass total at time (n) - mass total at time (n - 1) }\right]$$

$$\times \left[\text{ weight fraction glycol} \frac{(\text{time (n) + time (n-1)})}{2}\right]$$

$$= \text{Glycol Lost} \qquad (6.1)$$

6.1.4.1.1 Run 3: Resin AX/634 (see Appendix 2 Table 3)

$$[\,55.26 - 30.00\,] \times \left[\frac{0.0021 + 0.0044}{2}\right] = 0.08 \text{ kg}$$

$$[\,95.15 - 55.26\,] \times \left[\frac{0.0835 + 0.0021}{2}\right] = 1.71 \text{ kg}$$

$$[128.87 - 95.15\,] \times \left[\frac{0.1425 + 0.0835}{2}\right] = 3.81 \text{ kg}$$

$$[\,145.14 - 128.87\,] \times \left[\frac{0.1413 + 0.1425}{2} \right] = 2.31 \text{ kg}$$

$$[\,172.31 - 145.14\,] \times \left[\frac{0.1253 + 0.1413}{2} \right] = 3.62 \text{ kg}$$

∴ total glycol lost is 11.53 kg in 172.31 kg of distillate.

By knowing the initial glycol charged to the batch the losses can be assessed. If the quantity of distillate measured and the mass of glycol are known, then the percentage loss is calculable:

initial glycol charge:	2539 kg
distillate removed:	172.31 kg
glycol lost:	11.53 kg
actual water-off:	160.78 kg

∴ % glycol lost is

$$\frac{11.53}{2539} = 0.5$$

However, the reaction was not followed to completion and so the glycol losses may be higher. The expected water-off reaction for this resin is 358 kg. Since only 160.78 kg have been removed there is a lot of unreacted material remaining. As the reaction proceeds, the rate of glycol loss should be reduced since there will be less unreacted glycol in the reactor.

6.1.4.1.2 Run 4: Resin AY/395 (see Appendix 2 Table 4)

Substituting into equation 6.1:-

$$[\ 19.32 - 0.24\ ] \times \left[\frac{0.18 + 0.1706}{2} \right] \quad = \quad 3.35 \text{ kg}$$

$$[\ 50.70 - 19.32] \times \left[\frac{0.1585 + 0.18}{2} \right] \quad = \quad 5.31 \text{ kg}$$

$$[\ 75.55 - 50.70] \times \left[\frac{0.1488 + 0.1585}{2} \right] \quad = \quad 3.88 \text{ kg}$$

$$[\ 108.12 - 75.55\ ] \times \left[\frac{0.0897 + 0.1488}{2} \right] = \quad 3.88 \text{ kg}$$

$$[\ 148.11 - 108.12] \times \left[\frac{0.0246 + 0.0897}{2} \right] = \quad 2.29 \text{ kg}$$

∴ The percentage lost can now be calculated:-

initial glycol charge:	2456 kg
distillate removed:	556.52 kg
glycol lost:	18.64 kg
actual water-off:	537.16 kg

∴ % glycol lost:

$$\frac{18.64}{2456} = 0.8$$

The percentage glycol lost in the production of both resins is well within the 10% excess glycol in the initial charge weight. (The percentage loss for AX/634 may be higher, as the reaction was not monitored to completion. However, the glycol loss throughout the batch should still be within the 10% excess.) These values indicate that the partial condenser is operating efficiently (see section 6.2). The amount of water removed at the stage of reaction where monitoring of AY/395 ceased (ie 537.16 kg) indicates that the reaction has nearly reached completion. Calculations (using reactant charges and reactivities) show the expected water of reaction to be 545.9 kg. The actual water removed can be checked using the acid value recorded in Table 4 (Appendix 2).

6.1.4.1.2.1 Calculation of the Water of Reaction

When monitoring of the reaction had ceased, a total of 556.52 kg of distillate had passed through the meter. The reactant charges and reactivities suggest the water of reaction to be 545.9 kg. Earlier calculations (see section 6.1.4.1.2) have shown the glycol lost to be 18.64 kg and the water removed as 537.16 kg. Acid value calculations will reveal the true value for the water removed:

$$W = 18\,(X - Y - Z) \qquad 6.2$$

and

$$Y = \frac{AV\,(C - 18X + 18Z)}{56000 - AV.18} \qquad 6.3$$

where

C = the initial charge weight
X = the number of actual or potential molar carboxyl groups in the charge
Y = the number of molar carboxyl groups remaining after reaction
Z = the number of moles of anhydride present in the charge
AV = acid value
W = water of reaction.

Therefore, using the acid value in Table 4 of Appendix 2 (ie 55.5 mgkOH/g) and substituting into equations 6.2 and 6.3, the water of reaction can be calculated:-

$$Y = \frac{AV\,(C - 18X + 18Z)}{56000 - AV.\,18}$$

$$= \frac{55.5\,(6446 - 18(60.8) + 18(30.4)\,)}{56000 - 55.5\,(18)}$$

$$\therefore \qquad Y = 5.9$$

substituting for Y in equation 6.2:-

$$W = 18\,(X - Y - Z)$$

$$= 18\,(60.8 - 5.9 - 30.4)$$

$$\therefore \qquad W = 441 \text{ kg.}$$

Therefore, at the stage of leaving the reaction, 441 kg of water have been removed. However, the expected water-off is 545.9 kg and the water removed, as indicated by the flowmeter is 537.16 kg. The difference between the acid value and the expected results is due to the fact that the reaction still had a few more hours to process before reaching its specification. When the resin was within specification, the final acid value corresponded to 482.4 kg of water. Again, this value is lower than the expected value of 545.9 kg, but this value would be for the reaction to process to completion. If this occurred, ie processed to a very low acid value, the resin would gel. Therefore, the water removed at the final acid value stage will be a more realistic figure (ie 482.4 kg).

There still appears to be a discrepancy between the calculated values and those obtained from the flowmeter when the reaction was left.

ie Calculated distillate removed = mass water + mass glycol

= 441 + 18.64

= 459.6 kg.

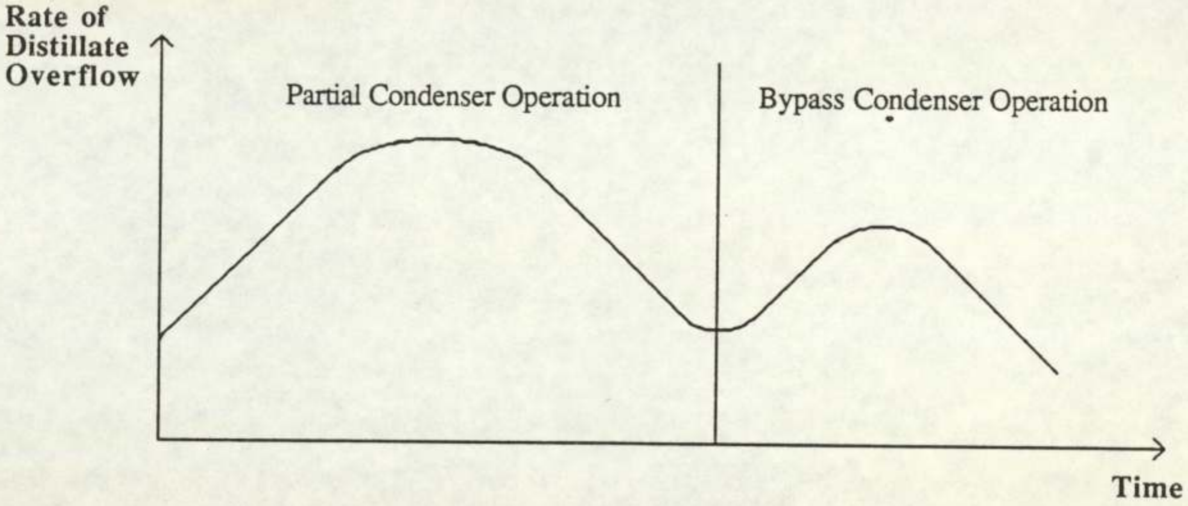
However, the distillate recorded by the meter at this stage is 556.52 kg. The higher than expected mass flow may be due to xylol losses (since the resin in run 4 was manufactured via the solvent process) or loss of water from the separator. Since xylol is immiscible with water (and the distillate samples are seen as homogenous mixtures), it appears that the excess may have come from the separator, ie the level in the separator can be lost if the vent becomes blocked with sublimed acid. The pressure of inert gas on top of the liquid in the separator will force water out of the overflow and into the distillate line (see figure 6.1). This will result in a higher than expected mass flow total recorded by the meter.

6.1.4.2 Distillation Profiles

Distillation rates were not examined for runs 1 and 2 due to blockages in the strainers and pipework associated with the mass flowmeter (see section 6.1.4.3).

However, runs 3 and 4 show variable distillate flowrates (see Appendix 2), which is unexpected since for a normal reaction/distillation stage a smooth curved profile is expected. The graphs of Appendix 2 should represent a section of the profile shown in figure 6.4.

Figure 6.4: Expected Distillation Profile



Graph 1 of Appendix 2 shows the distillate profile for run 3. Correlated with this graph in the Appendix is a plot (Graph 2) of the column top temperature from occasional observation. While it is in the process specification that this temperature should be maintained at 100°C to 105°C, the actual value was observed to vary considerably. There is some correlation between the two graphs of mass flowrate and temperature with time, ie when the temperature is allowed to rise, the distillate flowrate also rises. The glycol losses are also greater at times of high column top temperature. Observation of run 4 also showed an erratic distillate flowrate and composition. Column top temperature was not followed for this batch. However, the results confirm that the distillation profile is not always of the ideal smooth profile indicated in figure 6.4.

It is necessary to investigate how such erratic rates of distillation and temperature readings have occurred. The variation in flowrate cannot be due to the normal variation in profile which represents a smooth change. The high frequency of variation suggests that there is some external disturbance to the system of the same high frequency. There are two theoretical possibilities to account for external disturbances.

The first is the heat input. The oil system can in theory deliver heat at a higher rate through reduced oil demand and or higher temperature. (Reactors obtain their heat from an oil ring main which may introduce problems, eg reaching top temperature if all reactors are heating up or even maintaining top temperature.) However, the oil system serves only reactors whose combined demand for heating cannot vary at the frequency observed. If the temperature alone changed in the oil system, it is still unlikely to cause the variation in the distillation process. This is because vapour pressure in the reactor is a function of the batch temperature - it is not a function of heat into the batch. The batch is a large mass (approximately five tonnes) of resin in the reactor and so its temperature cannot change as quickly as the observed effect on distillate rate and column top temperature.

The other possibility is a variation in the cooling rate on the partial condenser. Manual control is used to maintain the column top temperature at approximately 105°C. In some cases a high flowrate is set and assumed constant. This introduces two problems. Firstly, the water to the condenser comes from a ring main and so varying demand in the rest of the system may reduce the flowrate and *vice-versa*. Secondly, the flowrates should be adjusted to maintain the distillation profile of figure 6.4. A more detailed discussion of partial condenser operation is included in section 6.2.

6.1.4.3 Line Blockages

The separator level has been found to fluctuate when the vent line blocks with sublimed acid (see section 6.1.4.1.2.1). Blockages were also encountered during the commissioning trials in the by-pass line and strainers. The by-pass line was opened and the strainers and process lines cleaned. The material removed appeared resinous and as such required identification. Infra-red analysis showed the material to be a resorcinol based resin. Prior to commissioning the mass flowmeter, the reactor had pressurised during the manufacture of this resin, resulting in release of resin into the overhead system. The by-pass column and associated pipework were found to be blocked and had to be cleaned before production could continue. Therefore, it may be possible that some resin remained and subsequent production washed this material through the lines to the mass flowmeter. After the lines and meter had been cleaned, further blockages were encountered in the meter for the by-pass line. The material, when removed from the by-pass line, appeared as a brown oil, which upon standing at room temperature showed precipitation of a white solid. When no distillate flows through the meter, ie between batches, the liquid in the sensor of the meter is allowed to stand and cool, resulting in precipitation of the white solid (thought to be the anhydride) and a blockage in the meter. The original design of the process lines enabled material in the by-pass line to pass through the meter, irrespective of whether or not the batch is monitored. This difficulty has been overcome by modifying the pipework so that material in the by-pass line can be re-directed to drain when the meter is not in use (see figure 6.1) and thus prevent sedimentation of the anhydride and ultimately blockages in the meter.

These blockages may affect the readings taken from the mass flowmeter by measuring zero flow in the case of a line blockage and surging flow in the case of a vent blockage. This must be taken into consideration when relying on the mass flowmeter for control purposes.

6.1.5 Conclusions

1 The mass flowmeter has been successfully commissioned. The error of the meter is within the repeatability error as specified by the manufacturer. The actual value of the error is difficult to quantify without very accurate analysis techniques.

2 The mass flowmeter was used to trace two distillation profiles and revealed inadequacies in control of the partial condenser (see section 6.2).

3 Glycol losses measured by the meter were well within the 10% excess glycol charged to the reactor (see section 6.2).

4 Numerous line blockages were experienced during the commissioning trials. Modification of the pipework to the meter should eliminate the resinous blockages. However, vent blockages due to sublimed anhydride may still be a problem.

5 Observations made during the trials strengthen the argument for automatic control of resin production, incorporating control of the partial condenser as the main feature (see section 6.2).

6.1.6 Recommendations

1 Use of the mass flowmeter as a control parameter to monitor the composition and rate of removal of distillate from reactor 5.

2 Control column top temperature with correct operation of the cooling water flow rates (see section 6.2).

3 Inform operators about vent blockages and their effect on mass flowmeter readings, ie ensure operators record any loss in the separator level on the log sheets.

6.1.7 Further Work

1. Collect mass flowmeter data to relate water-off to acid value and measure glycol loss.

2. Examination of vent blockages and possible prevention.

6.2 An Evaluation of the Performance of Reactor 5 Partial Condenser

6.2.1 Introduction

As outlined in section 6.1.4.2, insufficient control of the cooling water flowrates may result in erratic distillate flowrates recorded by the mass flowmeter. In addition to this, it had been suggested that reaction times for resins manufactured on reactor 5 via the fusion process (ie using the partial condenser) were extended, again possibly due to poor control.

The partial condenser was installed onto reactor 5 in February 1989. Although originally designed for reactor 4, it was expected that the partial condenser would operate satisfactorily on reactor 5, since both reactors are the same size. The partial condenser on reactor 6 is seen to perform satisfactorily, even though calculations[10] have shown it to be oversized. The partial condenser on reactor 5 is smaller than on reactor 6 (approximately 50%) and so an improved performance was expected.

(Note: Further calculations[10] have shown that the reactor 5 partial condenser is also oversized, ie the partial condenser designed for reactor 7 is smaller than the one on reactor 5, but the reactor has twice the capacity.)

The performance of reactor 5's partial condenser was monitored by comparison with the partial condenser on reactor 6.

6.2.2. Method

The performance of the partial condenser was measured by comparing log sheets for batches of the same resin manufactured on reactors 5 and 6 and recording:-

(i) Reaction time (ie heat on to heat off)
(ii) Cooling water flowrates
(iii) additions made during reaction (eg acid or glycol).

The following fusion process resins were chosen for analysis:-

AB
BE
AX (Stage I).

6.2.3 Results and Discussion

Table 6.2: Summary of Reaction Times for Resins Manufactured on Reactors 5 and 6

Resin	Mean Reaction Times ((hours)	
	Reactor 5	Reactor 6
AB	23.6	20.1
BE	29.1	19.7
AX (Stage I)	20.3	17.2

Note: Individual batch reaction times are recorded in Appendix 2a.

Table 6.2 shows the reaction times of resins manufactured on reactor 5 to be greater than those from reactor 6. A difference of up to 10 hours has been recorded.

eg: BE

The average reaction time for the manufacture of this resin on reactor 5 is 29.1 hours *cf* 19.7 hours on reactor 6. An increase in reaction time would be expected if water was being returned to the reactor from the partial condenser. (Polyesters are manufactured via an acid catalysed equilibrium reaction and rely on the removal of water to promote the reaction (see chapter 2).) Therefore the partial condenser on reactor 5 may be returning water to the reactor.

Both reactors (5 and 6) have the same capacity (ie 5 tonnes). However, the partial condenser on reactor 5 is approximately 50% smaller than the one on reactor 6. Earlier calculations have shown both condensers to be oversized. However, the smaller condenser on reactor 5 would be expected to perform more efficiently - this is not so!

6.2.3.1 Cooling Water Flow Rates and Their Influence on Reaction Times

6.2.3.1.1 AB

Table 5 of Appendix 2a shows how reaction times are influenced by the cooling water flow rate, eg extended reaction times appear to coincide with higher cooling water flow rates. These results are summarised in Table 6.3.

Table 6.3 Reaction Time (AB) *vs* Cooling Water Flow Rate

Batch No	Reaction time (hours)	Cooling Water Flow Rate (ltrs/hour)
866	30.00	800
867	20.25	400
886	20.00	500
888	27.00	1000

Table 6 of Appendix 2a records cooling water flow rates and reaction times for AB manufactured on reactor 6. The flow rates are much lower than those observed in the partial condenser of reactor 5. In fact, the highest flow rate recorded was 450 litres per hour.

The average reaction times for batches manufactured on reactor 5 is 23.4 hours *cf* 20.1 hours on reactor 6 (see Table 6.2). The increase in reaction time may be a result of high cooling water flow rates. The partial condenser of reactor 5 is smaller than on reactor 6, but operates with higher cooling water flow rates. (Note: both condensers are oversized and so cooling water flow rates become important.) Therefore, vapour in the condenser will be condensed, returning water (in addition to glycol) to the reactor and increasing reaction times. Extended reaction times are also observed for batches manufactured on reactor 5 with higher cooling water flow rates (see Table 6.3). Therefore, a reduction in the flow rate of the cooling water will be necessary to reduce the reaction times of AB manufactured on reactor 5.

The cooling water flow rate should be adjusted as temperature changes to maintain a column top temperature of approximately 105°C. However, for many batches of AB (and BE, AX Stage I - see later sections) the flow rate is set at the start of distillation, assumed constant and rarely adjusted. Section 6.1.4.2 shows this assumption may, in fact, be untrue, ie external factors may cause a reduction in the flow rate, resulting in a higher top temperature and subsequent removal of distillate (and hence glycol) from the reactor. If the flow rates are too high (as indicated in Table 6.2), extended reaction times are observed.

Table 6.4 Column Top Temperature *vs* Cooling Water Flow Rate

Batch No	Column top Temperature (°C)	Cooling Water Flow Rate (ltrs/hour)
800	99	1000
899	115	200

Table 6.4 illustrates the impact of manual control of the reactor 5 overhead system. Adjustments of the cooling water flow rates were not recorded for either batch. To maintain sufficient control of these batches, alterations of the cooling water flow rates would be required:

eg: batch 800 - requires a suitable reduction in its cooling water flow rate to obtain a column top temperature *cf* 105°C, whereas batch 899 will need an increase.

This problem may be associated with labour shortages experienced on the plant. There may, therefore, be a case for a suitable control loop that will automatically control column top temperature and cooling water flow rate. If this is not immediately possible, then suitable manual control will be required (see section 6.2.3.3), ie define reasonable flow rates to control column top temperature.

6.2.3.1.2 BE

Similar problems are experienced with the manufacture of BE, ie high cooling water flow rates in the partial condenser of reactor 5 result in condensation of water and increased reaction times (see Table 6.5).

Table 6.5 Reaction Time (BE) *vs* Cooling Water Flow rates

Batch No	Reactor	Reaction Time	Column Top Temperature (°C)	Cooling Water Flow Rate (ltrs/hour)
189	5	29.25	95	500
190	6	15.20	94	225

These results show the reaction times of consecutive batches of BE manufactured on reactors 5 and 6. Although the partial condenser on rector 5 is smaller than the one on reactor 6, it is seen to operate with a cooling water flow rate that is more than double the flow rate on reactor 6, at very similar column top temperatures. The high flow rate must be condensing the water, returning it to the reactor and increasing the reaction time. Alternatively, the indicated temperatures may not be representative of the actual vapour temperature, thus making difficulties in reaching conclusions.

6.2.3.1.3 AX (Stage I)

Production of this resin is a two-stage process. However, the second stage incorporates the solvent process and was therefore not examined.

Reaction times were again extended, due to higher than necessary cooling water flow rates in the partial condenser of reactor 5 (see Table 6.6.).

Table 6.6 Reaction Time (AX (Stage I)) *vs* Cooling Water Flow Rate

Batch No	Reactor	Reaction Time	Column Top Temperature (°C)	Cooling Water Flow Rate (ltrs/hour)
625	6	18.50	99	225
627	5	23.75	100	900
630	5	21.25	101	1000
631	6	16.75	100	450

Table 6.6 shows an unusual correlation between column top temperature and cooling water flow rate for reactors 5 and 6, ie at similar column top temperatures the flow rate on reactor 5 is at least twice that on reactor 6. The result is increased reaction times for resins manufactured on reactor 5 due to the condensation and return of water to the reactor.

An additional point of interest is the variation in the flow rates used in the partial condenser of reactor 6, eg the cooling water flow rate of batch 631 is double the flow rate of batch 625 at very similar column top temperatures. Further work may, therefore, be required to optimise the performance of the reactor 6 partial condenser.

6.2.3.2 Effectiveness of the R5 Partial Condenser

Glycol losses have been identified if a batch requires a glycol addition. This may not be strictly accurate since a 10% glycol excess is charged to each batch. A more accurate method would be to analyse the distillate using the mass flowmeter. However (for the purposes of this project), glycol additions were used to indicate glycol losses from the system (see Table 6.7).

Table 6.7 Summary of Batches Requiring Glycol or Acid Additions

Resin	Reactor 5			Reactor 6		
	Glycol	Acid	Total No Batches Studied	Glycol	Acid	Total No Batches Studied
AB	1	8	17	1	4	9
BE	7	0	7	7	0	7
AX (Stage I)	0	0	6	7	0	19

Glycol losses from R5 appear minimal, since very few additions were required:-

eg: 1 batch of resin AB from 17 batches studied, and no batches of AX.

However, BE required glycol additions for every batch studied on reactors 5 and 6. This may be attributable to the resin chemistry rather than the design of the overheads.

As mentioned earlier, the cooling water flow rates on the R5 partial condenser are higher than necessary. It is, therefore, unlikely that the system will lose, glycol, since the majority of vapour is condensed and returned to the reactor.

Further examination of glycol losses will be required if and when control of the cooling water is optimised. Glycol losses could be accurately monitored using the mass flowmeter now installed in the R5 distillate line. Glycol losses from R6 appear greater than R5 since more batches required additions.

The addition of acid to approximately 50% of batches of AB manufactured on reactors 5 and 6 indicates that the system is retaining its glycol charge. There is, therefore, the capacity to make more resin, or the glycol charge may be reduced.

6.2.3.3 Manual Control of the Reactor 5 Partial Condenser

As mentioned in section 6.2.3.1.1, there appears to be little or no control of column top temperatures with respect to cooling water flow rates in the partial condenser, resulting in increased reaction times. To overcome this problem, a control loop is required to maintain the column top temperature of 100°C to 105°C with automatic adjustment of the cooling water flow rates, should the top temperature stray outside this range. However, if this is not immediately possible, then suitable manual control is required in the short term.

Using the data collected in section 6.2.3.1 the following control was introduced to improve operation of the partial condenser and hopefully productivity of the reactor:

For all batches of resin manufactured on reactor 5 via the fusion process:
At the start of distillation set the cooling water flow rate to the partial condenser at 400 - 500 litres/hour and adjust as necessary:
eg:

(i) If the column top temperature rises above 105°C, increase the cooling water flow rate to 600 - 800 litres/hour.

(ii) If the column top temperature falls below 100°C, reduce the cooling water flow rate to 0 - 300 litres/hour.

NB: Record the cooling water flow rates and any adjustments on the log sheets.

The effect of this manual control on the reaction times can be seen in Table 6.8.

Table 6.8 The Effect of Manual Control on Reaction Times

Resin	Reaction Time (hours)			
	Batch No	Before Control	After Control	Improvement in Productivity (%)
AY	513	34.5	24.0	30
BE	199	30.4	18.75	38
BE	200	30.4	17.5	42

All three batches show a reduction in their reaction times, and hence an improvement in productivity, as a result of the manual control introduced to the reactor 5 partial condenser. Examination of subsequent batches manufactured via the fusion process on reactor 5 may be required to ensure that suitable control has been introduced. Further improvements in productivity may be observed if or when an automatic control loop is installed.

6.2.4 Conclusions

1 Resins manufactured via the fusion process on reactor 5 show extended reaction times when compared to those from reactor 6.

2 Extended reaction times were seen to be caused by higher than necessary cooling water flow rates in the partial condenser of reactor 5.

3 There appears to be little/no correlation between column top temperature and the cooling water flow rates of reactor 5, resulting in either increased reaction times (if the flow rates are too high) or glycol losses (if the flow rates are too low, see section 6.1.4.2).

4 The result of conclusions 1 to 3 was to introduce manual control on the partial condenser of reactor 5. This was seen to improve productivity of the reactor by an average of 37% for resins manufactured via the fusion process.

6.2.5 Recommendations

1 Introduce automatic control of column top temperature and cooling water flow rates of the reactor 5 partial condenser.

6.2.6 Further Work

1 Monitor reaction times of resins manufactured via the fusion process on reactor 5 using the manual control introduced in section 6.2.3.3.

2 Examine the operation of the reactor 6 partial condenser and improve control.

6.3 References

9 Private communication:- Cartlidge, P; Sims, J; "Reactor 5 Commissioning Report, Appendix B, Teaching Company Progress Report, 13 December 1988 to 20 March 1989".

10 Private communication:- Cartlidge, P; Sims, J; "Teaching Company Progress Report, 20 March 1989 to 24 May 1989".

11 Private communication:- Peacocke, C; Scott, J; "Final Year Industrial Report, Aston University, 20 October 1989, to 15 December, 1989.

APPENDICES TO SECTION 2

CHAPTER 6

APPENDIX 2

TABLE 1

RESULTS: RUN 1

DATE: 15/11/89
BATCH: Resin AY/375
REACTOR 5

Time (Real)	Mass Total (Kg)	Mass Flow (Kg/Min)	Density (g/cc)	Total Volume of Distillate (l)	Distillate Temperature (°C)	Reactor Temperature (°C)	Column Top Temperature (°C)
0115	0	0	0.9977	0		163	99
0130	-0.04	-0.04	0.9980	-0.04	13.2	164	96
0145	-0.08	0	0.9980	-0.08	13.3	164	96
0200	-0.11	0	0.9975	-0.11	13.4	164	96
0215	5.94	0	0.9997	5.94	18.2	164	96

TABLE 2

RESULTS: RUN 2

DATE: 17/11/89
BATCH: Resin AB/928

REACTOR 5

Time (Real)	Mass Total (Kg)	Mass Flow (Kg/Min)	Density (g/cc)	Reactor Temperature (°C)
1230	0.17	0.29	0.9920	155
1255	54.65	3.80	0.9875*	160
1330	165	3.93		167
1400	240.2	3.12		172
1500	302.2	0.1		172
1535	351	0.26		180
1600	356	1.3		184
1630	408	1.0		186
1700	437	0.75		191
1730	460	0.84		196
1800	480	0.6	0.9908	200
1830	489.43	0.4	0.9900	
1900	496.75	0.3	0.9913	

* :26 error came up

TABLE 3

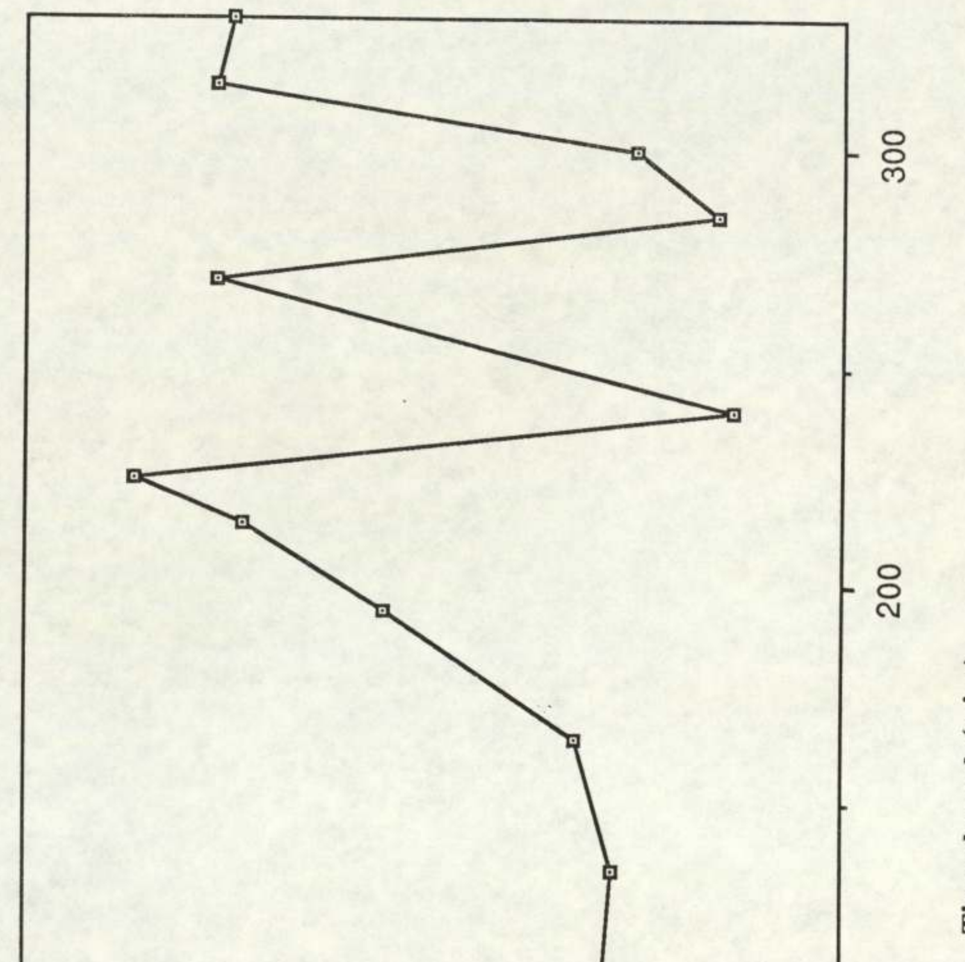
RESULTS: RUN 3

DATE: 1/12/89
BATCH: Resin AX/634
REACTOR 5

Time (Real)	Mass Total (Kg)	Actual Water Off (Kg)	Mass Flow (Kg/Min)	Density (g/cc)	Distillate Temperature (°C)	Column Top Temperature (°C)	Sample No	Composition % Weight Prop Glycol
1200	0.12		0.07	0.9994	14.3			
1217	2.86		0.16	0.9994	14.0			
1230	7.45		0.44	0.9995	13.9			
1245	15.64		0.52	0.9992	14.5			
1300	19.77		0.22	0.9993	14.1			
1315	22.09		0.13	0.9994	13.7		1	0.44
1345	30.00		0.44	0.9996	13.9			
1415	43.02	55.18	0.42	0.9993	14.1	105	2	0.21
1445	55.26		0.49	0.9995	13.8			
1515	74.44	93.32	0.84	1.0007	13.9	155	3	8.35
1535	95.15		1.10	1.0064	14.4			
1545	105.35		1.30	1.0106	15.0	115		
1600	115.52	137.19	0.20	1.012	13.8	120	4	14.25
1630	128.87		1.15	1.0115	14.9	105		
1645	141.02	160.73	0.23	1.0114	13.7		5	14.13
1700	145.14		0.38	1.0114	13.2	110		
1715	158.30		1.15	1.0106	14.9		6	12.53
1730	172.31		1.12	1.01	14.8			

APPENDIX 2

Graph 1 ; Mass flow variation with time:- Run 3



APPENDIX 2

Graph 2 ; Column top temperature variation with time:-Run 3

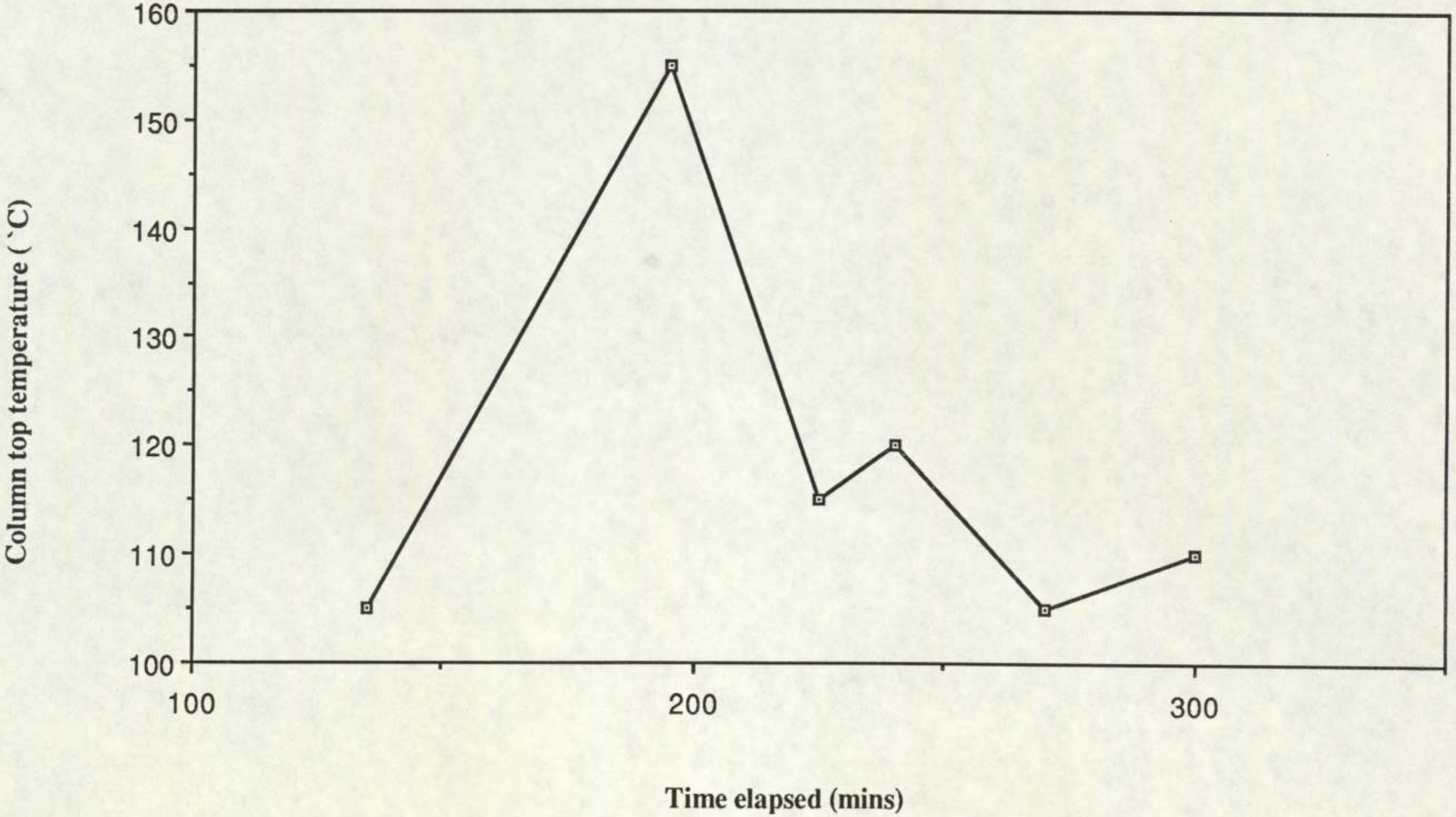


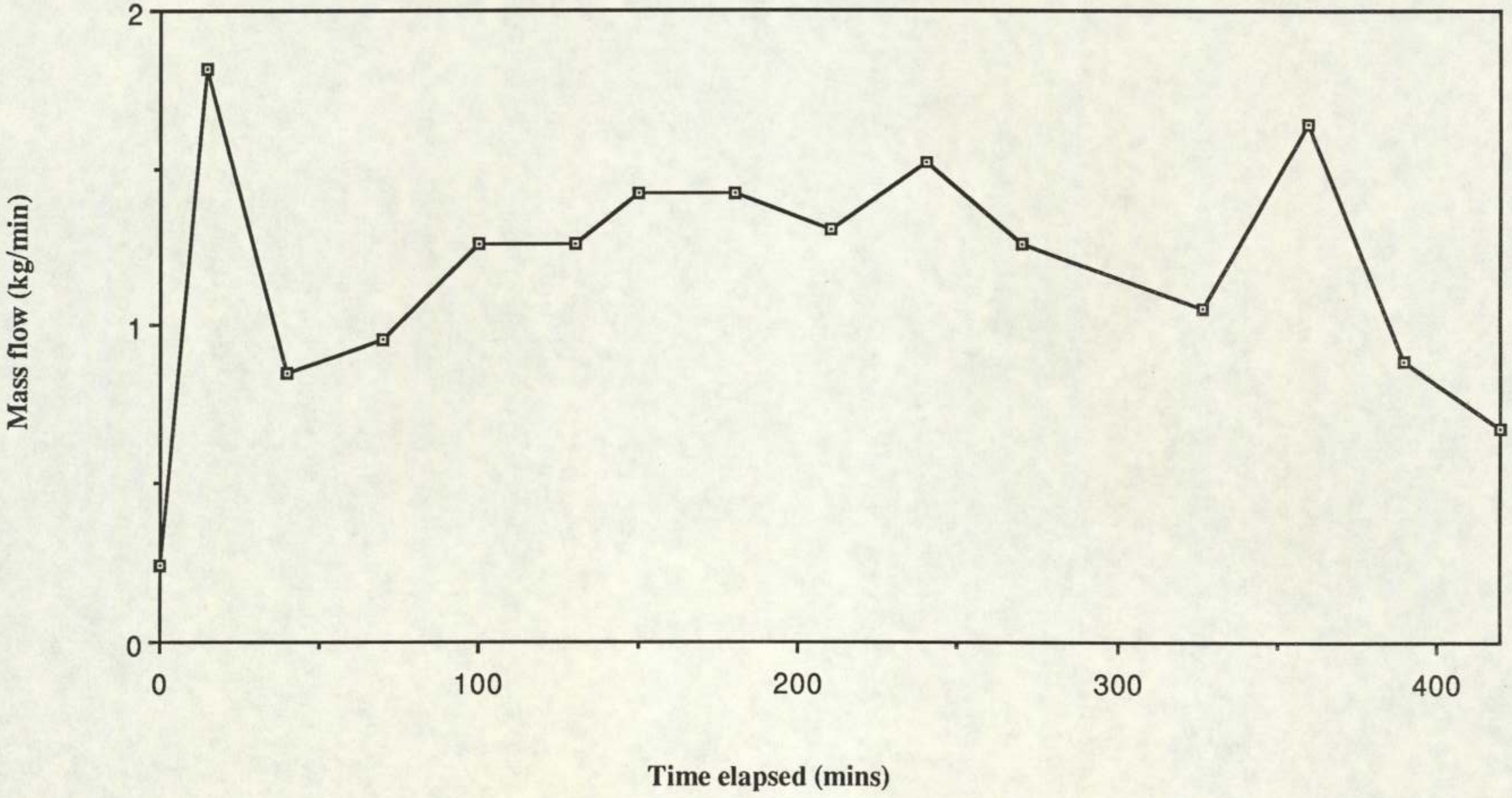
TABLE 4

RESULTS: RUN 4

DATE: 4/12/89
BATCH: Resin AY/395
REACTOR 5

Time (Real)	Mass Total (Kg)	Actual Water Off (Kg)	Mass Flow (Kg/Min)	Density (g/cc)	Distillate Temp (°C)	Column Top Temp (°C)	Reactor Temp (°C)	Composition % Weight Prop Glycol	Acid Value (mgKOH/g)
1210	0.24	0.24	0.24	1.0112	21.4	96	164	17.06	
1225	19.32	15.98	1.82	1.0105	24.0	98	165	18	
1250	50.70	42.04	0.85	1.0092	23.2		165	15.85	
1320	75.55	63.08	0.96	1.0084	23.3		165	14.88	
1350	108.12	91.76	1.26	1.0034	23.8		167	8.97	
1420	148.11	129.47	1.26	0.9992	23.2		172	2.46	
1450	188.72	170.08	1.42	0.9966	25.8		176		
1520	245.65	227.01	1.42	0.9961	26.9		181		
1550	290.62	271.98	1.31	0.9953	27.4		185		
1620	340.95	322.31	1.52	0.9948	28.4		190		
1650	377.93	359.29	1.26	0.9951	30.7		193		
1747	440.63	421.99	1.06	0.9946	37.9		202		
1820	497.68	479.04	1.64	0.9935	38.8	105	206		
1850	532.74	514.1	0.89	0.9949	35.9	107	210		
1920	555.80	537.16	0.68	0.9959	33.3	112	214		
	556.50								55.5

Graph 3 ; Mass flow variation with time:- Run 4



APPENDIX 2a

Table 5	AB	Reactor 5
Table 6	AB	Reactor 6
Table 7:	BE	Reactor 5
Table 8	BE	Reactor 6
Table 9:	AX (Stage I)	Reactor 5
Table 10:	AX(Stage I)	Reactor 6

Note:

The cooling water values recorded are the initial flow rates recorded by the plant and the time for which they remained at that flow rate.

These flow rates may be adjusted to maintain the column top temperature between 100-105°C.

There may be some fluctuation in the flow rates due to changes in demand on the ring main system.

APPENDIX 2a

TABLE 5 **Resin Type: AB** **Reactor 5**

			Cooling Water		Additions	
Batch No	Reaction Time (hrs)	Column Top Temperature (° C)	Flow Rate (ltrs/hr)	Time (hrs)	Glycol (ltrs)	Acid (kg)
864	20.25	105	600	4.0		
866	30.00	104	800	5.0		
867	20.25	105	400	3.5		
870	21.75	105	500	0.5		
886	20.00	101	500	3.5		
888	27.00	99	1000	5.0		100
893	27.50	100	850	1.0	120	50
896	25.25	100	1000	1.0		
898	20.25	103	200	5.5		
899	23.00	115	200	0.5		
928	21.75	112	100	5.5		50
933	23.25	100	900	5.5		60
934	24.50	100	1000	2.5		50
935	24.00	103	400	4.5		120

TABLE 6 **Resin Type: AB** **Reactor 6**

Batch No	Reaction Time (hrs)	Column Top Temperature (° C)	Cooling Water Flow Rate (ltrs/hr)	Cooling Water Time (hrs)	Additions Glycol (ltrs)	Additions Acid (kg)
861	17.25	92	180	1.0		
879	23.25	98	315	3.0		
884	23.25	105	135	4.5	50	
911	21.75	95	450	6.0		100
914	15.75	94	not recorded	-		
916	21.25	92	405	4.5		50
918	18.75	90	270	4.0		60
919	22.00	90	not recorded	-		110
924	18.00	107	225	0.5		

TABLE 7 **Resin Type: BE** **Reactor 5**

Batch No	Reaction Time (hrs)	Column Top Temperature (° C)	Cooling Water		Additions	
			Flow Rate (ltrs/hr)	Time (hrs)	Glycol (ltrs)	Acid (kg)
182	23.00	104	450	6.5	50	
183	27.00	97	500	8.5	60	
185	32.50	100	not recorded	-	60	
186	30.75	101	not recorded	-	105	
187	30.25	92	not recorded	-	75	
188	31.25	96	100	2.5	60	
189	29.25	95	500	3.5	50	

APPENDIX 2a

TABLE 8 **Resin Type: BE** **Reactor 6**

			Cooling Water		Additions	
Batch No	Reaction Time (hrs)	Column Top Temperature (° C)	Flow Rate (ltrs/hr)	Time (hrs)	Glycol (ltrs)	Acid (kg)
184	16.75	98	not recorded	-	145	
190	15.20	94	50	7.0	90	
191	23.25	90	180	2.0	36	
192	24.25	95	180	3.0	25	
193	20.00	90	not recorded	-	50	
194	19.00	91	not recorded	-	60	
195	19.50	93	not recorded	-	40	

APPENDIX 2a

TABLE 9 **Resin Type: AX (Stage 1)** **Reactor 5**

			Cooling Water		Additions	
Batch No	Reaction Time (hrs)	Column Top Temperature (° C)	Flow Rate (ltrs/hr)	Time (hrs)	Glycol (ltrs)	Acid (kg)
602	18.00	107	1100 - 1400	11.0		
604	18.00	105	2000	12.5		
605	19.00	107	1500	14.5		
627	23.75	102	900	17.5		
630	21.25	104	1500	16.5		
634	21.75	103	1000 - 1500	15.5		

APPENDIX 2a

TABLE 10 **Resin Type: AX (Stage 1)** **Reactor 6**

			Cooling Water		Additions	
Batch No	Reaction Time (hrs)	Column Top Temperature (° C)	Flow Rate (ltrs/hr)	Time (hrs)	Glycol (ltrs)	Acid (kg)
609	16.75	102	360 - 450	13.0		
610	16.50	103	450	12.0		
611	16.75	106	450 - 562	12.5	135	
612	16.50	103	495 - 765	12.5	45	
615	15.50	105	450 - 810	11.0	50	
616	16.25	99	337 - 900	12.0		
617	19.50	102	315 - 405	14.5		
618	15.50	102	450 - 675	11.0		
619	18.00	104	135 - 540	12.0		
620	16.00	103	450 - 585	11.0	90	
621	15.50	104	562 - 675	12.0	45	
623	19.50	104	180 - 360	14.0		
624	16.00	102	450 - 900	12.0		
625	18.50	104	225 - 675	13.0	30	
626	17.00	102	495 - 630	13.0	45	
628	16.50	105	450 - 900	11.5		
629	16.75	100	450 - 540	12.5		
631	16.75	102	360 - 450	13.0		
633	23.50	102	675 - 1125	19.0		

NB The cooling water flow rates are the range used throughout the reaction, due to continual adjustments of the flow rate.

SECTION 3

CHAPTER 7

SETTLING OF FUMED SILICA FROM THIXOTROPIC POLYESTER RESINS

7 SETTLING OF FUMED SILICA FROM THIXOTROPIC POLYESTER RESINS

7.1 Introduction

Problems were noted with regard to the settling of the thixotropic agent, fumed silica, from the BIP reprocessed resin, R. As a result, commercial difficulties arose. Fumed silica is dispersed into resin R by means of an ultrasonic homogeniser. The cause of settling is likely to be over or under dispersion of the fumed silica, thus questioning the efficiency of the homogenising unit.

The aim of the project was to identify the cause of settling and subsequently optimise the operation of the equipment used in the dispersion of fumed silica, in order to obtain a consistent saleable product.

7.2 The Principles of Production Used in the Manufacture of Resin R

The thixotropic properties of this resin are provided by fumed silica (see section 7.2.2), which is dispersed into the base resin by means of an ultrasonic homogeniser (see section 7.2.1). The equipment used in the production of this resin is illustrated in the simplified flow diagram of figure 7.1.

Approximately twenty tonnes of base resin are charged to Blender 2. Agitation begins upon addition of the initial additive. Once the required additives have been charged, the fumed silica is "wetted-in" (ie mixed into the resin with mild agitation) for one hour prior to reflux. Refluxing of the blender contents through the ultrasonic homogeniser then takes place in two stages. The first stage of reflux continues for four hours, at the end of which a second series of additives is charged to the blender. The resin is continuously refluxed through the homogeniser during the second charging stage and then for a final four hours. Therefore, each batch of resin R spends approximately eight hours refluxing through the homogeniser. At the end of the second stage, the resin is tested (see Chapter 4) and if within specification, will be run off.

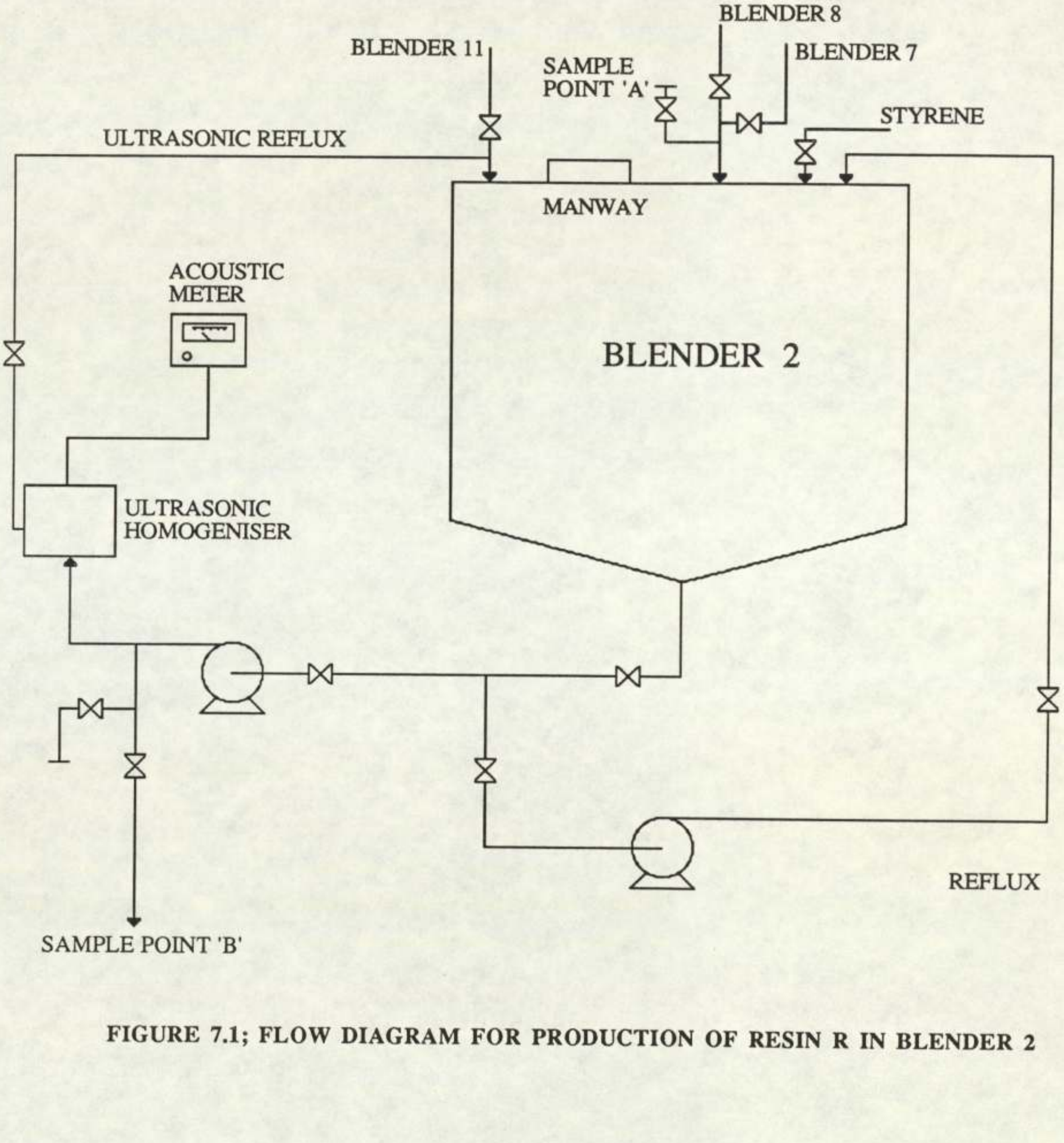


FIGURE 7.1; FLOW DIAGRAM FOR PRODUCTION OF RESIN R IN BLENDER 2

7.2.1 Ultrasonic Homogenisation

BIP use ultrasonic homogenisation to disperse thixotropic agents, such as fumed silica, into several of their polyester resins.

The ultrasonic homogeniser is an in-line machine and is used when the required degree of dispersion cannot be achieved by high speed mixing equipment. In addition, the homogeniser has the ability to produce fine dispersions without air entrainment or heat build-up. When functioning efficiently, the homogeniser should disperse the thixotropic agent to a level where settling out is eliminated.

7.2.1.1 Mode of Operation[12]

A schematic diagram of the homogeniser attached to Blender 2 may be seen in figure 7.2.

Process material is fed by pump into the homogenising head, where it is forced at high velocity through a specially formed orifice. The emerging flat stream is bisected by a blade which is caused to vibrate by the process material flowing over it. The relationship between orifice and blade is critically controlled to optimise blade activity. The blade vibrates at ultrasonic frequencies which generate intense cavitation (see section 7.2.1.2) within the resin, eliminating the energy losses which normally occur when energy is transferred from one medium to another. It is this cavitation, the compression and rarefraction of small gas or vapour nuclei within the resin which causes most of the dispersion effects in the process material.

The required operating pressure (400 to 450 psi) and throughput are determined by the use of different size orifices or jets, whereas the velocity is changed to achieve the necessary degree of dispersion.

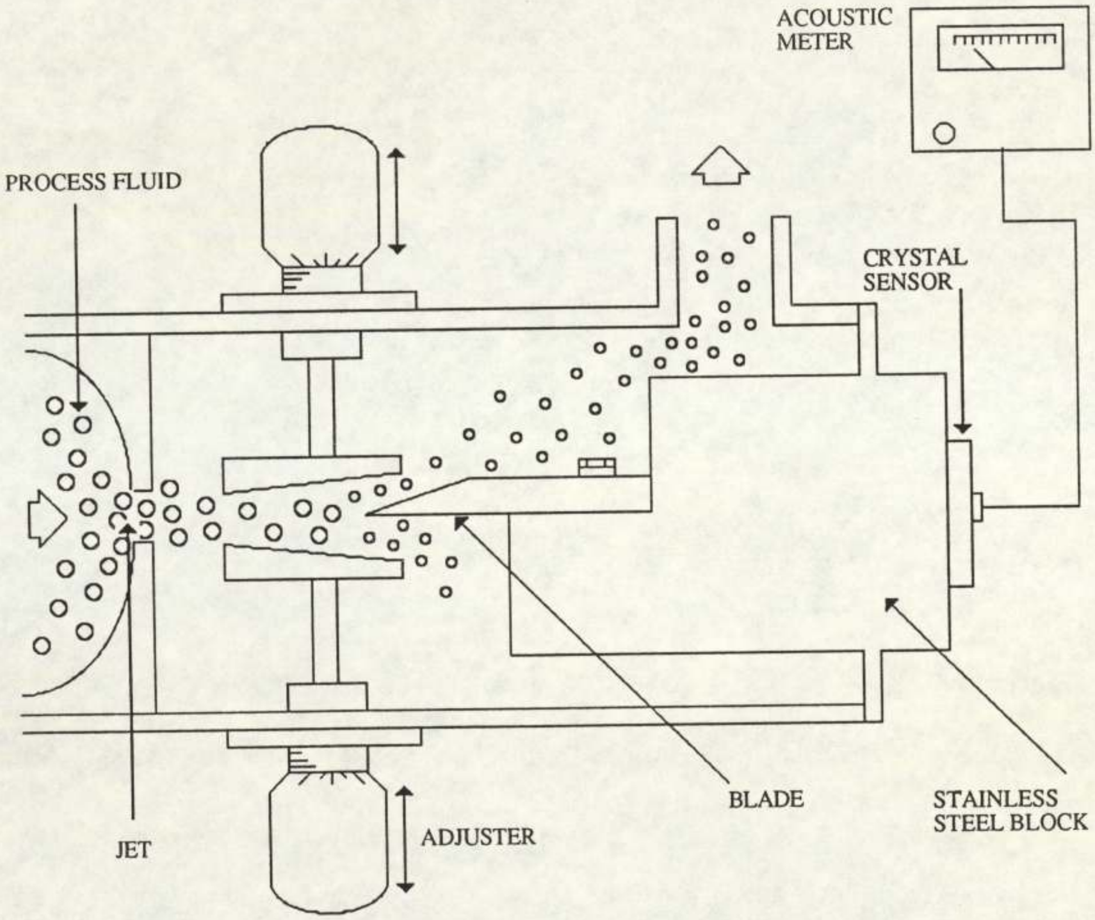


FIGURE 7.2; ULTRASONIC HOMOGENISER ATTACHED TO BLENDER 2

7.2.1.2 Cavitation

The propagation of ultrasonic sound waves through a liquid medium is accompanied by the formation of cavities, or bubbles, within the medium. The production of these cavities and the effect they induce is called cavitation[13]. Two main types of cavitation bubble can exist within a liquid medium:

(i) containing gas previously dissolved in the liquid, and
(ii) containing the vapour of the liquid medium.

Cavitation of the first type occurs as gases are liberated from the walls of the vessel containing the liquid and also from the face of the sound generator employed. The bubbles formed are of a size easily visible to the naked eye.

Cavitation bubbles containing the vapour of the liquid medium are of a much smaller size and shorter life. Cavities of this type are generally only formed in liquids which are not aerated. There is evidence to support the existence, to a lesser extent, of a third class of cavitation bubble which is more or less a complete void.

7.2.1.2.1 Mechanism of Cavitation

The full development of cavitation by ultrasonic energy is a step by step process, each step being dependent for its commencement on the previous phase. There exists a number of distinct cavitation phases, provided the necessary pre-initiation condition of the liquid is met.

(i) Pre-initiation conditions of the liquid:

The initiation of cavitation requires the presence of permanent gas nuclei in the liquid. These nuclei are carried by liquid streaming into the highest intensity area of the sound field and provide weak spots around which cavitation may take place. In addition to gas nuclei, the presence of solid particles in the liquid medium may aid cavitation.

(ii) Initiation phase of cavitation:

The initiation phase begins when a nucleus of low enough strength enters the high intensity area. The gas/vapour filled cavities of these nuclei are expanded and contracted by the cyclic tension (rarefraction) and compression caused by the sound waves in the surrounding medium. As the nucleus moves towards highest sonic concentration, its volume oscillates with the frequency of the sound wave. The cavity gradually grows larger for several tenths of a millisecond, or during several hundred cycles of oscillation at the frequency used. Upon reaching its resonant size, the cavity enters its catastrophic phase.

(iii) Catastrophic Phase:

At its resonant size, the cavity shows a sudden increase in amplitude of vibration but at the same excitation frequency. The vibration is no longer sinusoidal and the cavity begins to collapse. In the case of a vapour filled cavity, the walls of the cavity are forced inwards until they impinge on the small nucleus of vapour contained within. High localised temperatures and pressures can be produced (up to 13000°F and 75000 psi, respectively) during cavitation. However, their duration is extremely brief and they are minutely localised. The violent periodic vibration radiates intense shock waves of an amplitude largely exceeding that of the originating action. These shock waves are responsible for most of the cavitation phenomena induced by ultrasonic means. During this phase the violently vibrating cavity streams along and out of the core of high intensity. Nothing further is visible until a new burst is initiated.

Figure 7.3 illustrates a cavitational burst.

The effect of cavitation depends on the energy level of the imploding bubbles as well as the number of bubbles per unit volume. Cavitation density may be increased by raising the level of ultrasonic excitation. Raising the hydrostatic pressure suppresses the number of cavitational events, but substantially increases the shock intensity of individual bubbles. Cavitational shock intensity is also a function of bubble size, which increases with the period of excitation frequency.

As ultrasonic frequency is increased, the production of cavitation in liquids becomes more difficult, requiring more acoustic power. Cavitation is more intense at lower frequencies and ceases altogether in the high MHz range. The most probable explanation for this is that at high frequencies, where the rarefraction and compression half cycles are very short, the finite time required at normal acoustic power levels for a bubble to grow sufficiently to rupture the liquid completely, is not available. Since it is necessary to overcome the cohesive forces within a liquid to form a vapour filled cavity, it is probable that cavitation is more difficult to achieve in viscous liquids (high cohesive pressure). This may be one of the causes of the marked differences which exist in cavitational intensity of different liquids at equal acoustic pressures.

Cavitation is also related to vapour pressure, the amount of dissolved gases, and, of course, the presence of gases and other nuclei that determine its onset.

7.2.1.3 The Function of the Thixotrope

A thixotropic fluid is one in which the application of shear forces (eg stirring or shaking) causes a reduction in viscosity of the fluid. However, on removal of the applied stresses, the viscosity returns to its former level as a function of time.

Thixotropic agents are utilised for their ability to induce thixotropic properties to many resin products. Prior to gelation, they provide a high enough viscosity to prevent the resin from sagging or draining from vertical mould surfaces.

7.2.1.3.1 Mechanism of Thixotropy

The mechanisms involved with the thixotropic properties observed when fumed silica is used as a thixotrope are not complex, involving merely the formation and breaking of hydrogen bonds[14].

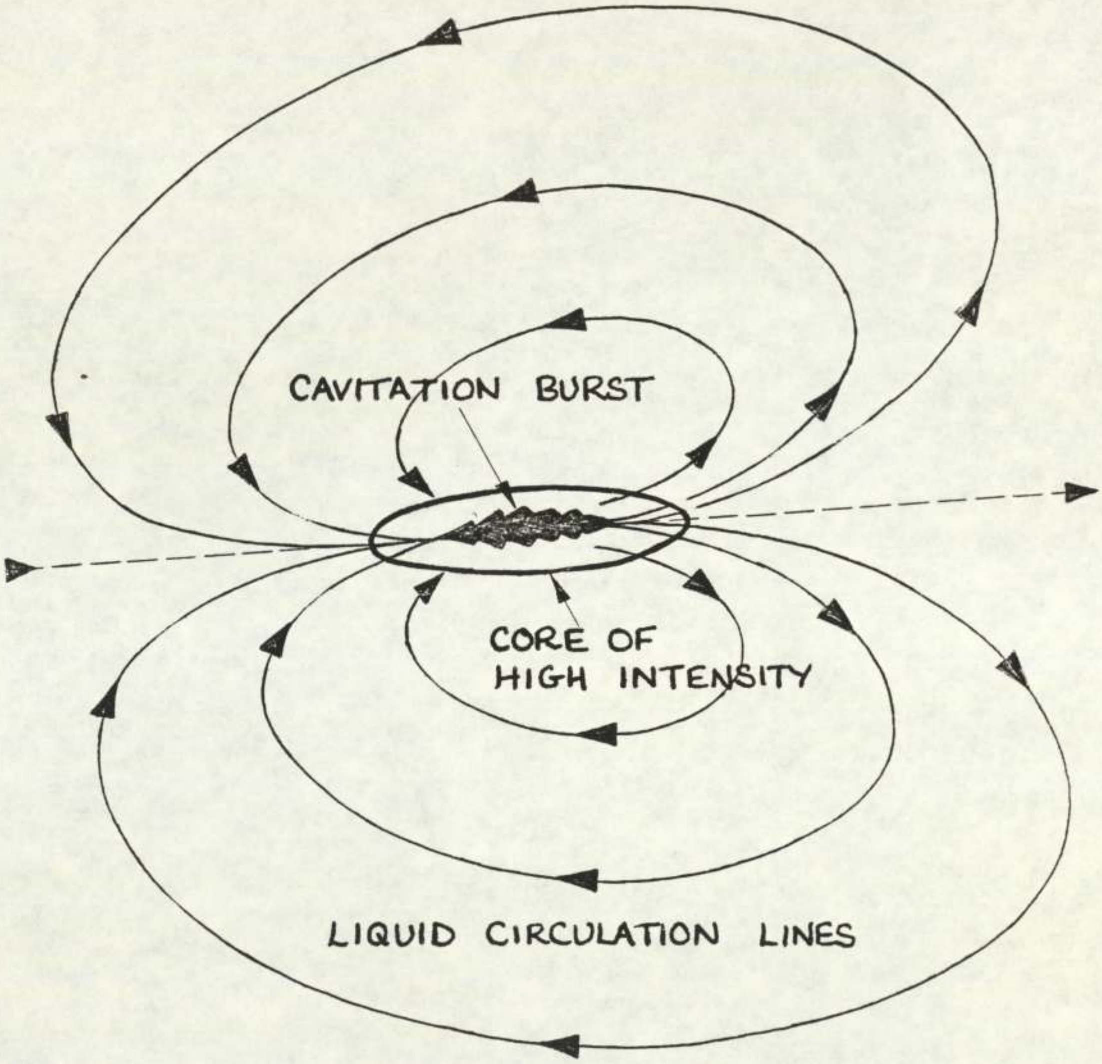
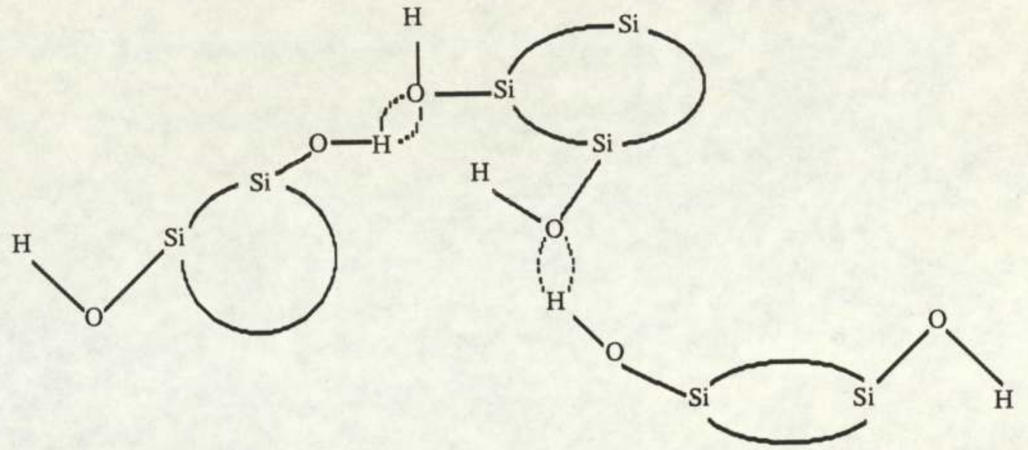


FIGURE 7.3 **REPRESENTATION OF CAVITATION BURST AND LIQUID CIRCULATION PATHS**

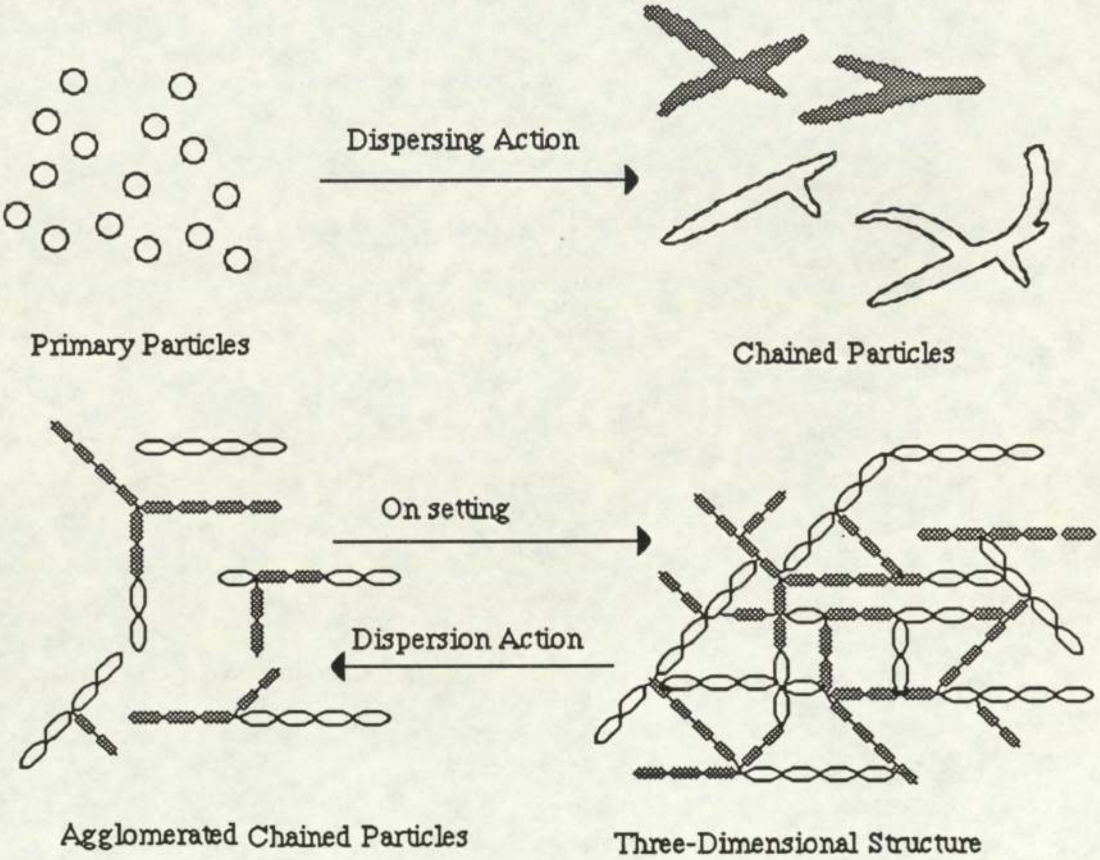
Aggregate particles of fumed silica have many covalently bonded silanol (SiOH) groups on their surface. When dispersed each particle of silica may interact with others. Hydrogen bonding between silanol groups on the surface of adjacent silica particles leads to the build up of a three-dimensional network of silica particles (see figure 7.4).

Figure 7.4: Hydrogen Bonds Between Fumed Silica Particles



The result of such a process is an increase in viscosity. However, hydrogen bonds are easily broken by mechanical effects and the application of shear will break down the three-dimensional structure, resulting in a reduction of viscosity. On removal of the applied shear, the chain structure of the dispersed silica particles reforms as a function of time, until the viscosity eventually returns to its former level (see figure 7.5).

Figure 7.5: Formation of the Three-Dimensional Structure

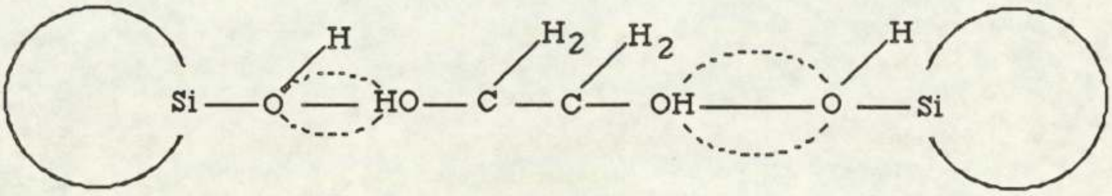


An ideal thixotropic system will behave as described. However, many factors exist which could affect the efficiency of fumed silica as a thixotrope:

(i) nature of the medium
eg viscosity and polarity. Less polar liquids are more easily thickened.

(ii) presence of short chain polyfunctional materials or additives.
eg ethylene glycol is thought to enhance thixotropy by acting as a bridging agent between two fumed silica aggregates which may have been too far apart to interact (see figure 7.6).

Figure 7.6: Interaction of Two Fumed Silica Aggregates via an Ethylene Glycol Bridge



This may become important if the base resin contains any unreacted (free) glycol (see Chapter 8).

(iii) Degree of dispersion of silica. Silica may be over or under dispersed.

(iv) The presence of water in small amounts (1% to 2%) promotes thixotropy. As more water is added, the silica particles are forced further apart. Fewer hydrogen bonds are formed, leading to reduction in viscosity of the system.

7.3 Procedure

Two batches of resin R, 92 and 95, manufactured in Blender 2 were examined to observe the efficiency of dispersion of the fumed silica within the resin.

For each batch a 1 lb sample was taken via the manway on top of the blender (sample A) and from the sample point just before the homogenising unit (sample B) - see figure 7.1.

Samples were taken directly before the start of reflux and thereafter every hour until the end of second stage reflux.

Whenever possible, the operating frequency of the homogeniser was recorded during a batch, using the acoustic meter supplied with the unit.

The samples collected from batches 92 and 95 were examined to investigate the following properties[15] :

(i) Thixotropic Index

- Ferranti Shirley Viscometer (see Chapter 4).
- Haake Viscometer.

(ii) Particle Size/Distribution

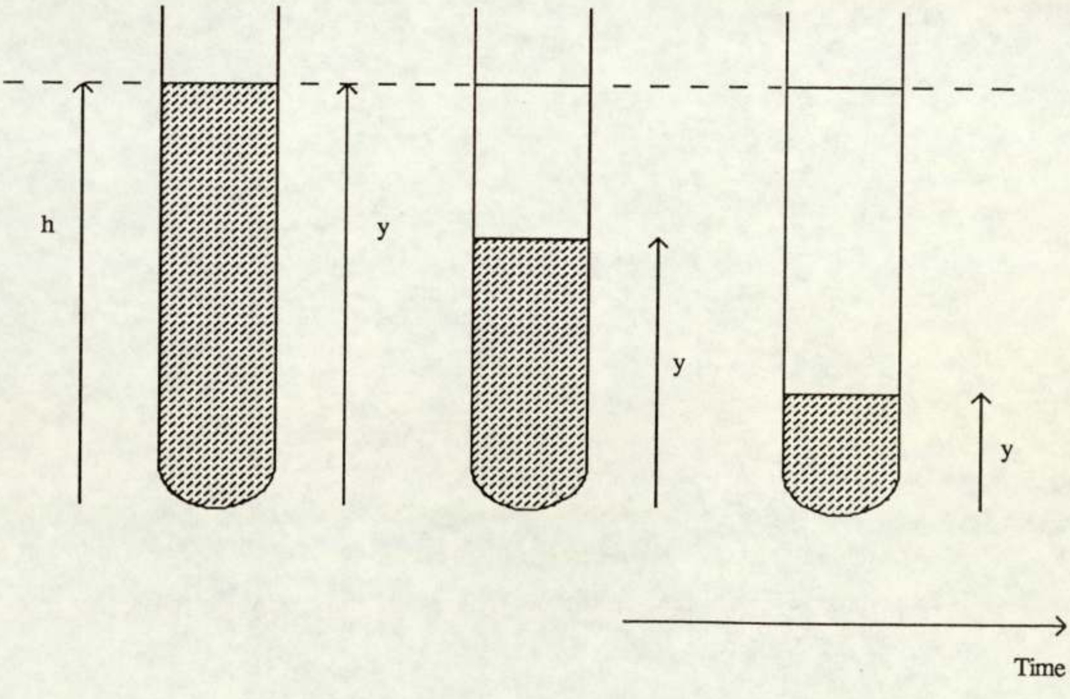
- Malvern Particle Size Analyser (see Appendix 3c).
- Scanning Electron Microscope.
- Optical Microscope.

(iii) Settling

- Graduated Test Tubes (see below).

Resin samples taken at intervals throughout the blending cycle were poured into graduated test tubes and any separation that took place was recorded (see Tables 1 and 2 of Appendix 3b for identification of samples). After pouring the samples into the graduated test tubes, the time, date, height of resin in test tube (h) and height of any sedimentation boundary (y) were recorded and monitored regularly,

ie



Plots of relative height (y/h) versus sedimentation time were made for each sample.

7.4 Results[15] and Discussion

The Haake Viscometer, Scanning Electron Microscope and Optical Microscope techniques proved fruitless due to problems during analysis, eg both microscopic methods revealed nothing about the degree of dispersion of fumed silica in the base resin, whereas the Haake Viscometer was very time consuming with respect to the number of samples.

7.4.1 Thixotropic Index

A number of plots were produced (see Appendix 3, Graphs 1 to 4) relating thixotropic index to batch time.

(i) Batch 92

A gradual increase in thixotropy is observed with time (see graphs 1 and 2). Such an increase is expected, since the degree of dispersion of fumed silica increases. There is, however, a sudden decrease in the thixotropic index value for the sample taken from the bottom of blender 2 after 12 hours. A plot of viscosities at the two-shear rates was made and showed a viscosity measurement which does not follow the trend. Thus the "dip" in thixotropic index may be due to experimental error in measuring the viscosity at 3 rpm.

It may also be possible that the sample taken at this stage was not a true representation of the batch, since 1 lb samples were used to represent a 20-tonne batch. Samples taken for the purposes of this project came from the sample line before the homogeniser and from the top of the blender via the manway (see figure 7.1). No direct comparisons can be made between resin character directly before and after the ultrasonic homogeniser, due to inadequate sampling facilities. The installation of a sample line after the homogenising unit is required to provide a more accurate representation of the equipment's performance. However, the method of sampling used did reveal a difference in the resin characteristics between the top and bottom of the blender (see also section 7.4.2 and 7.4.3).

(ii) Batch 95

Samples taken from the top of blender 2 show a gradual increase in thixotropy, up to 7 hours of refluxing, after which there was a sharp drop below the required specification of 1.15 (see graph 3). The increase in thixotropy is related to the increase in dispersion of fumed silica, ie as dispersion increases, the primary silica particles form chained particles which can hydrogen bond eventually to form a three-dimensional network (see figure 7.5). It is the gradual formation of this network that provides the increase in thixotropy. However, the sudden reduction in thixotropy after 7 hours of refluxing may be as a result of over dispersion, ie physical degradation of bonds within the silica network may occur, resulting in a loss of thixotropy. Such a trend would be observed if the resin was refluxed for too long or at a lower than necessary frequency (cavitation is more intense at lower frequencies). Further work is required to optimise the reflux time and frequency to prevent any over dispersion. It is also possible that under dispersion (although not seen here) can take place, through insufficient reflux time and/or a high frequency. Under dispersion will also result in low thixotropy as the chained particle system (and subsequently the three-dimensional network) is not established.

7.4.2 Particle Size/Distribution

See Appendix 3c for the principles of particle size measurement.

Use of the Malvern Particle Size Analyser showed a very clear trend in particle size distribution, examples of which are given in figures 1 and 2 of Appendix 3a. An elongation of the size distribution as batch time progressed indicated that size reduction was taking place.

eg Batch 92

Before reflux (see figure 1), most particles are seen to have a diameter of approximately 100 μm. However, after the second stage reflux, a shift towards a smaller particle size is observed (see figure 2). Such a trend is expected, since the action of homogenisation will disperse the large primary silica particles. The result is smaller particles which can hydrogen bond to form the three-dimensional network (see figure 7.5). The stirred cell of the analyser (see Appendix 3c) will prevent any chain build up and so smaller particles (as a result of increased dispersion) will be observed. Figure 2 also indicates that some of the particles remain at their initial size, ie before the start of reflux, the diameter of many particles is approximately 100 µm. However, at the end of the second stage (although the overall particle size is seen to reduce), some particles remain at their original (size 100 µm), probably as a result of under dispersion.

7.4.3 Sedimentation of Fumed Silica

Graphs 1 to 4 of Appendix 3b show the plots of relative height (y/h) versus sedimentation time for each sample taken from he top and bottom of blender 2.

(i) Batch 92

All samples taken from the top of blender 2 began to settle within 25 days of the test (see Graph 1). Sample 18A, taken at the end of the second stage reflux, has settled significantly, whereas sample 14A (after four hours' reflux) shows very little sedimentation.

In contrast, samples taken from the bottom of blender 2 (see Graph 2), for the first stage of reflux, began to settle within five days of the test. However, none of the second stage samples settled, but they did exhibit phase separation/settling lower down in the test tubes.

Sedimentation will occur if the fumed silica is over or under dispersed because in each case the three-dimensional structure is not formed (see section 7.2.1.3.1). As a result the silica particles are unable to support each other and sedimentation occurs.

Phase separation (seen in second stage reflux samples taken from the bottom of blender 2) may also result from a poor dispersion technique, eg some samples were seen to contain air bubbles, which can become attached to silica particles, causing them to float. Since sedimentation occurs at the same time, phase separation is observed, ie a clear region in between two turbid areas.

(ii) Batch 95

No significant sedimentation is seen in samples 22A, 23A and 25A (ie three, four and five hours, respectively, into reflux) during the 25 days of the test. However, the later and final product samples all began to settle 15 days into the test. Earlier samples (particularly 20A, after one hour reflux) were also seen to settle within a relatively short time period, eg 20A started to settle immediately. These observations strengthen the argument of poor dispersion within the system, eg settling in early samples may result from under dispersion, whereas over dispersion may cause settling in the later samples.

A similar trend is observed in samples taken from the bottom of the blender, ie initial and final product samples (20B and 27B, respectively) exhibit significant separation, whereas the intermediate samples show little or none (see Graph 4).

Plots correlating Relative Height (the measurement of settling) with Reflux Time (see Graphs 5 and 6 of Appendix 3b) show an apparent relationship between the two, ie there appears to be an optimum time after which sedimentation increases again - eg Batch 95 (see Graph 6): the first five hours of reflux show a reduction in sedimentation after which there is a marked increase.

This suggests that reflux times require a modification to optimise the process and reduce settling. In the early stages, settling appears to result from under dispersion, whereas over dispersion may be the problem in the later stages. More data is required and the settling or phase separation lower down than at the surface must somehow be taken into account.

There is a distinct difference in settling rates between the top and bottom samples taken at the same time, thus showing, not surprisingly, that the resin at the top and bottom of the blender differ. This may become important when the resin in drummed-off, since it may be possible that different drums contain resin with slightly different properties, eg thixotropy.

Other observations were made on problem areas within the process which could contribute to the unsatisfactory nature of products from blender 2:

(i) The total raw materials charge to blender 2 for the production of resin R is about 23000 kg. With a pump delivering material at the rate of 5000 kg/hr, the ultrasonic homogeniser will treat a full blender charge in just over 4.5 hours. However, since the homogeniser discharge is refluxed back to the blender, which is then continuously agitated, and each batch runs for at least eight hours, it is safe to assume that some material passes through the homogeniser more than once. There is also the probability that a fraction of product does not pass through the homogeniser at all. This was confirmed by the Malvern Particle Size Analyser, which indicated extreme size reduction from some particles while others remained at their initial size. Sedimentation (see section 7.4.3) and loss of thixotropy (see section 7.4.1) also indicate poor dispersion. Hence, resin R manufactured on blender 2 is likely to be a mixture of over and under dispersed material.

(ii) Delays may occur in charging the second stage additives, eg batch 92 has a 12-hour reflux cycle, compared to the 8 hours quoted in the manufacturing instructions. This delay is not only expensive to the company in terms of "dead time" for the blender, but also with regard to the possible damage this may cause the product. The continuous refluxing of the blender contents through the ultrasonic homogeniser during the second charging stage could lead to over dispersion of the fumed silica.

(iii) An interesting revelation concerns the ultrasonic homogeniser itself. The unit was installed about one and a half years ago. No information was discovered to relate the arrival of the unit with the onset of settling problems. The suppliers, Lucas Dawe Ultrasonics, designed the equipment with reference to the material it would handle. An operating pressure of 400 to 450 psi was recommended. All indications suggest that this recommendation was ignored and that no work was done to correlate operating pressure with frequency to obtain an optimum acoustic frequency range. An acoustic frequency meter was supplied with the homogeniser, which was then tuned to run at the maximum meter reading. Since then the unit has been run under the assumption that "highest is best", a proposition which research into cavitation has shown to be untrue. Checks with the acoustic meter indicated the tendency of the setting to stray over a period of time, prompting retuning. The installation of a permanent meter would enable plant operators to see if the unit was set correctly.

It may be useful to conduct further tests once the homogeniser has been optimised with regard to pressure and frequency.

(iv) An investigation into the resin chemistry may be required:

eg examination of the order and rate of addition of the numerous additives involved in the formulation of this resin, to observe what effect, if any, this has on sedimentation of fumed silica.

7.5 Conclusions

1 The settling problems associated with the manufacture of resin R on blender 2 are caused by over and under dispersion of the process material. Overall it is most likely to be over-dispersed.

2 The ultrasonic homogeniser is incorrectly tuned and may not be operating at the required pressure.

3 Other contributing factors which may result in an inconsistent and unreliable product are:-

(i) variable batch times

(ii) insufficient agitation of the blender contents after completion of homogenisation.

7.6 Recommendations

1 Subsequent to this work a meter to monitor the operating pressure of the homogeniser was installed, resulting in an immediate and dramatic improvement in product quality.

2 Install a permanent acoustic meter for use with the ultrasonic homogeniser and include regular frequency checks in the manufacturing instructions for each product.

3 Standardise batch times, ie do not reflux between the first and second stages.

4 Install a sample line after the homogeniser.

5 Modify the reflux system to prevent air entrainment in the resin.

7.7 Further Work

1 Correlate operating pressure and acoustic frequency of the homogeniser with product settling, in order to determine the optimum operating conditions for the ultrasonic homogeniser.

2 Repeat the trials when a new sample line (after the homogeniser) has been installed.

3 Examine the cause(s) of air entrainment in the resin.

7.8 References

12 Lucas Dawe Ultrasonics, North Street, Bradford, West Yorkshire, BD1 4UB; "Ultrasonic Homogenisation".

13 Eusminger, D; "Ultrasonics, the Low and High Intensity Applications".

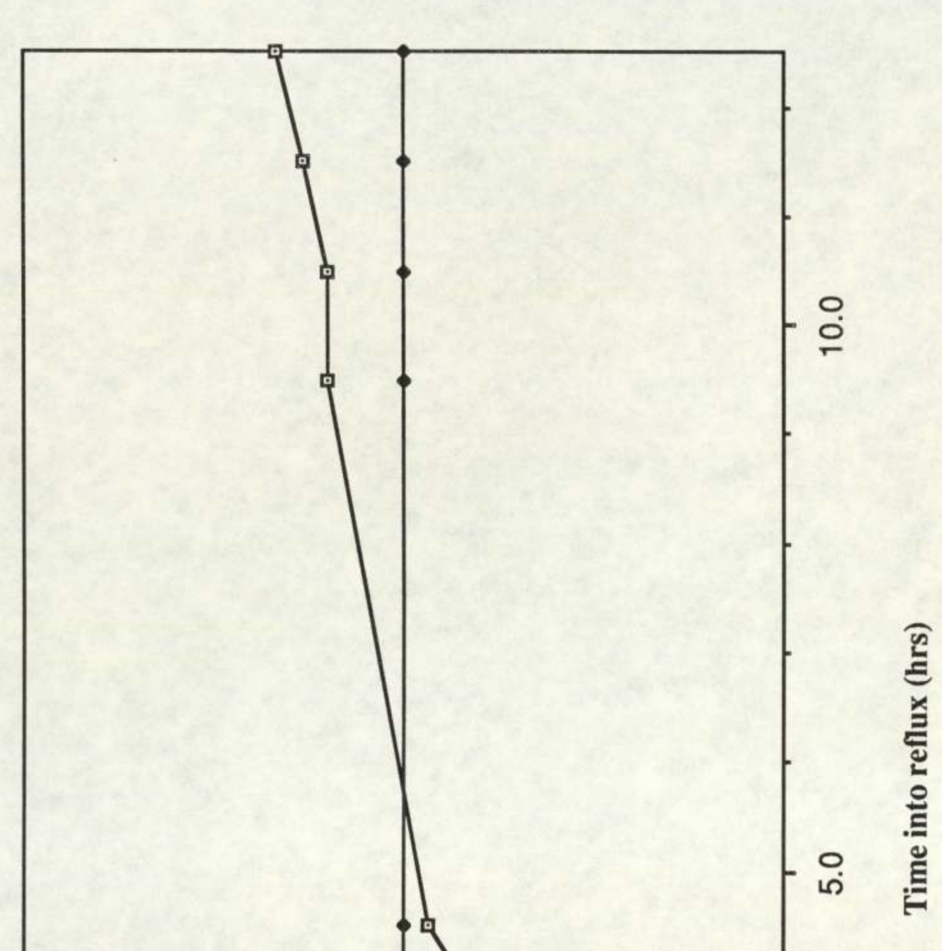
14 Pearlman, D J, Cabot Corporation; "Dispersing Fumed Silica In Liquid Systems".

15 Nicholls, R D, Sayed A A; "Final Year Industrial Project, Aston University, 1989".

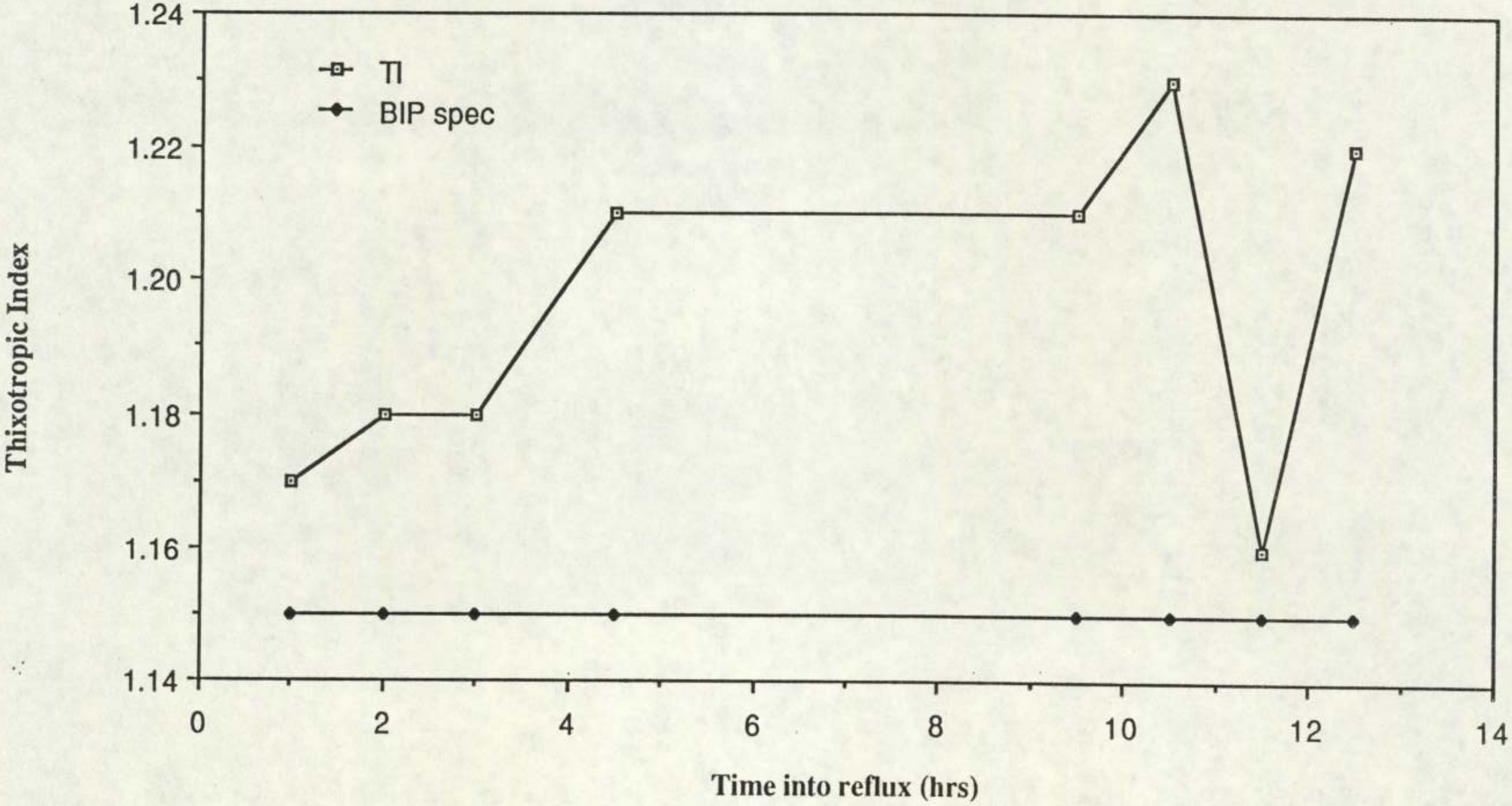
APPENDICES TO SECTION 3

CHAPTER 7

Graph 1; Fluctuation in TI with Processing Time,Top of Blender 2

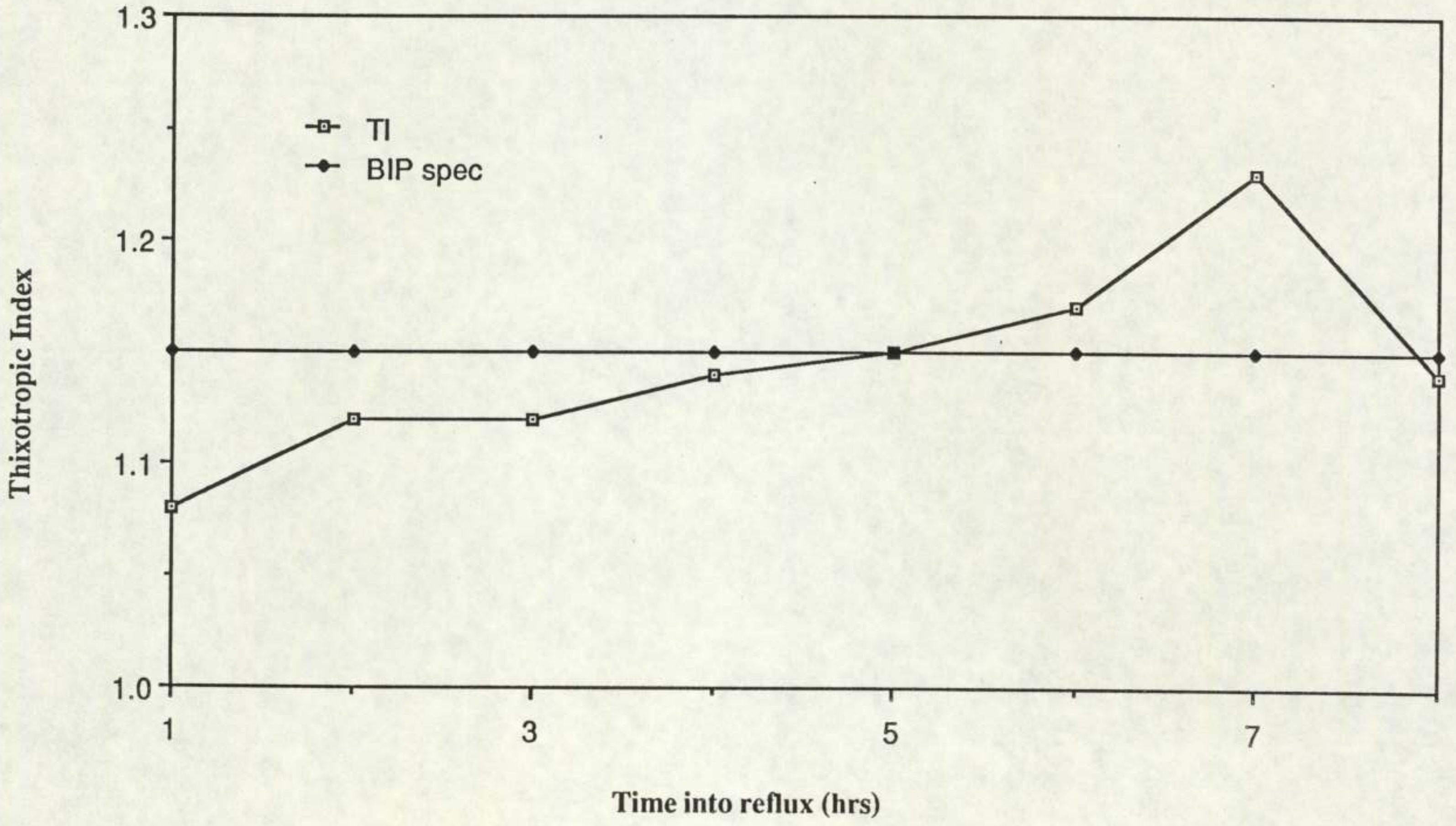


Graph 2; Fluctuation in TI with Processing Time, Bottom of Blender 2



APPENDIX 3

Graph 3; Fluctuation in TI with Processing Time, Top of Blender 2



Graph 4; Fluctuation in TI with Processing Time, Bottom of Blender 2

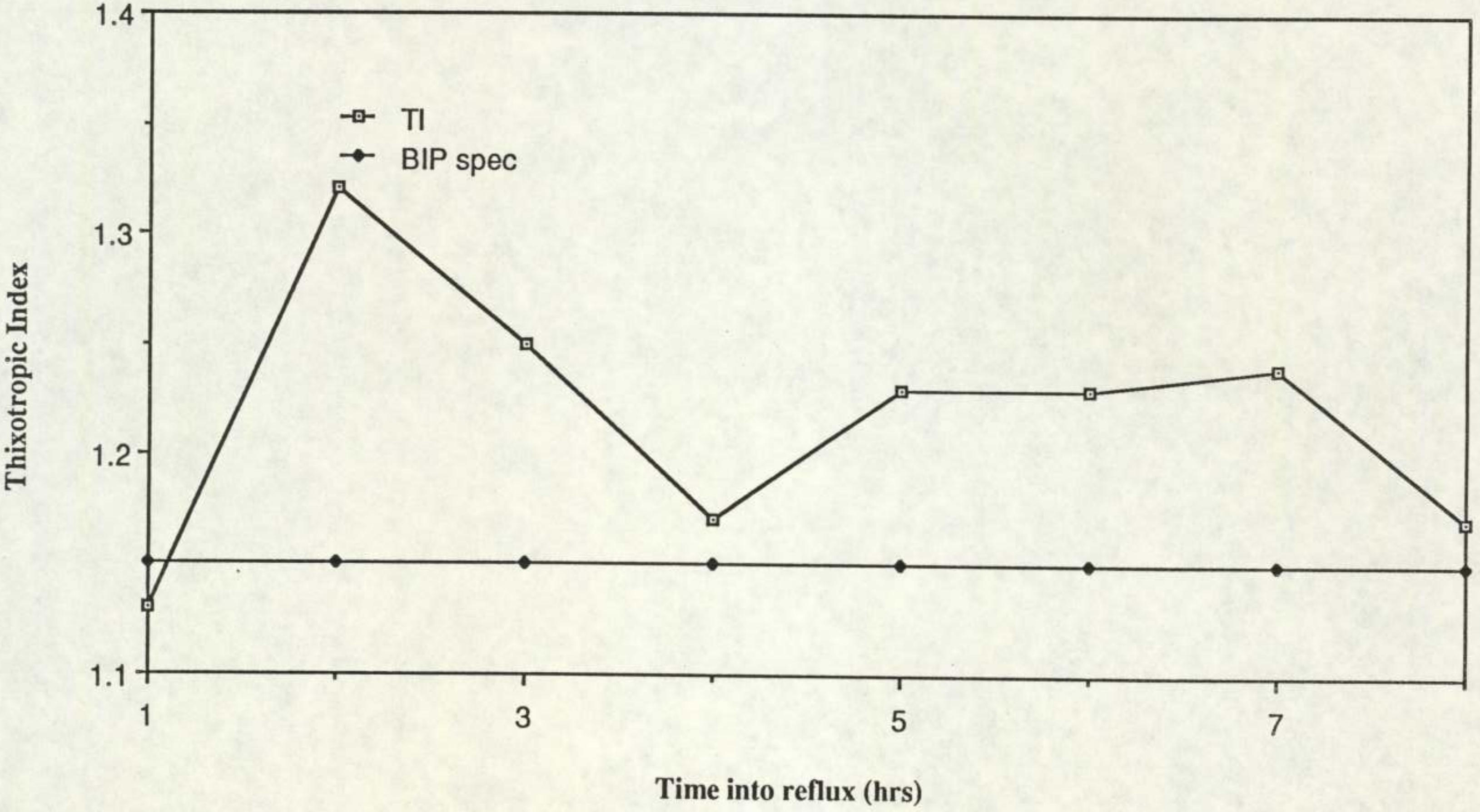


FIGURE 3a.1

APPENDIX 3a

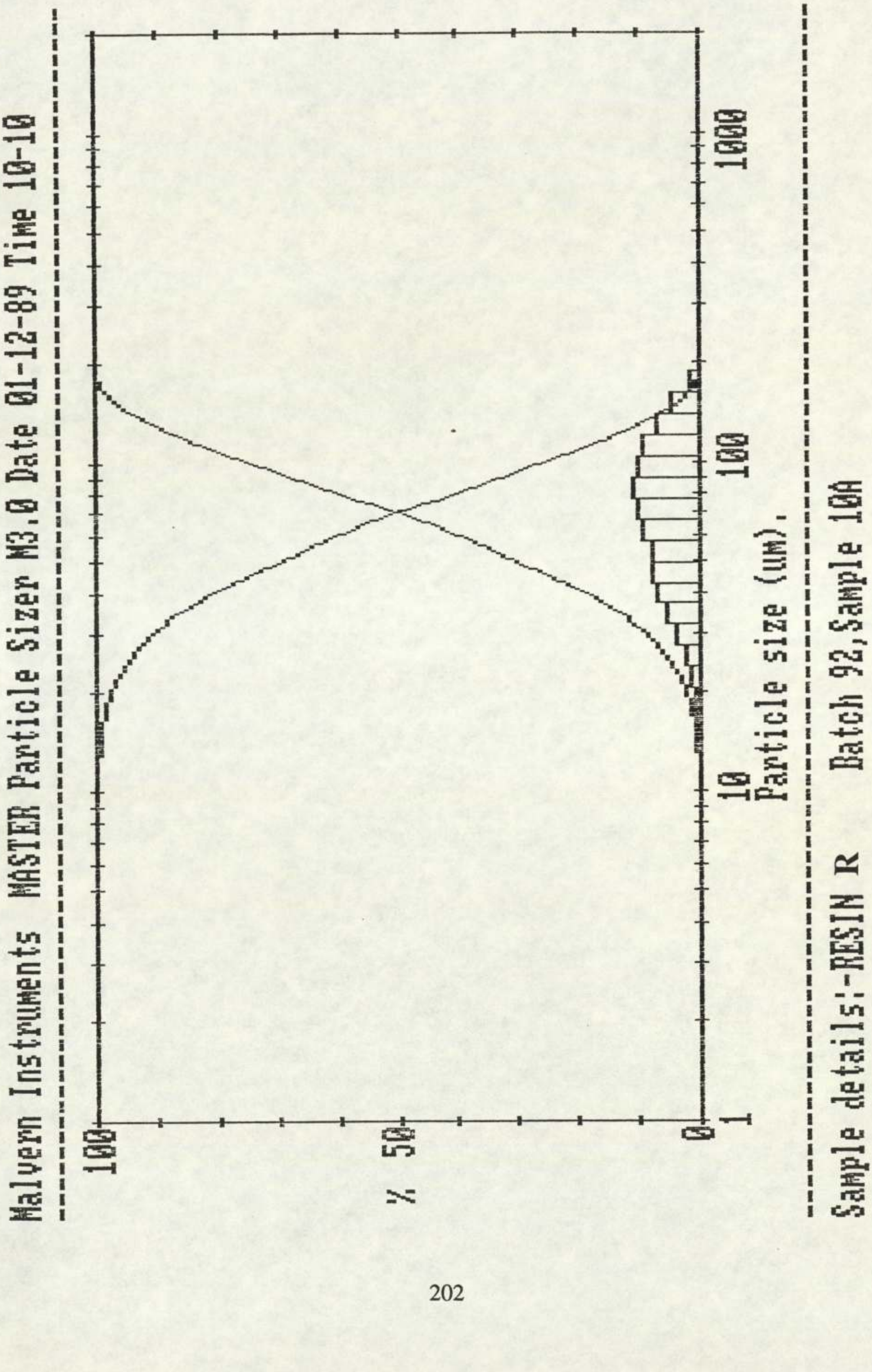
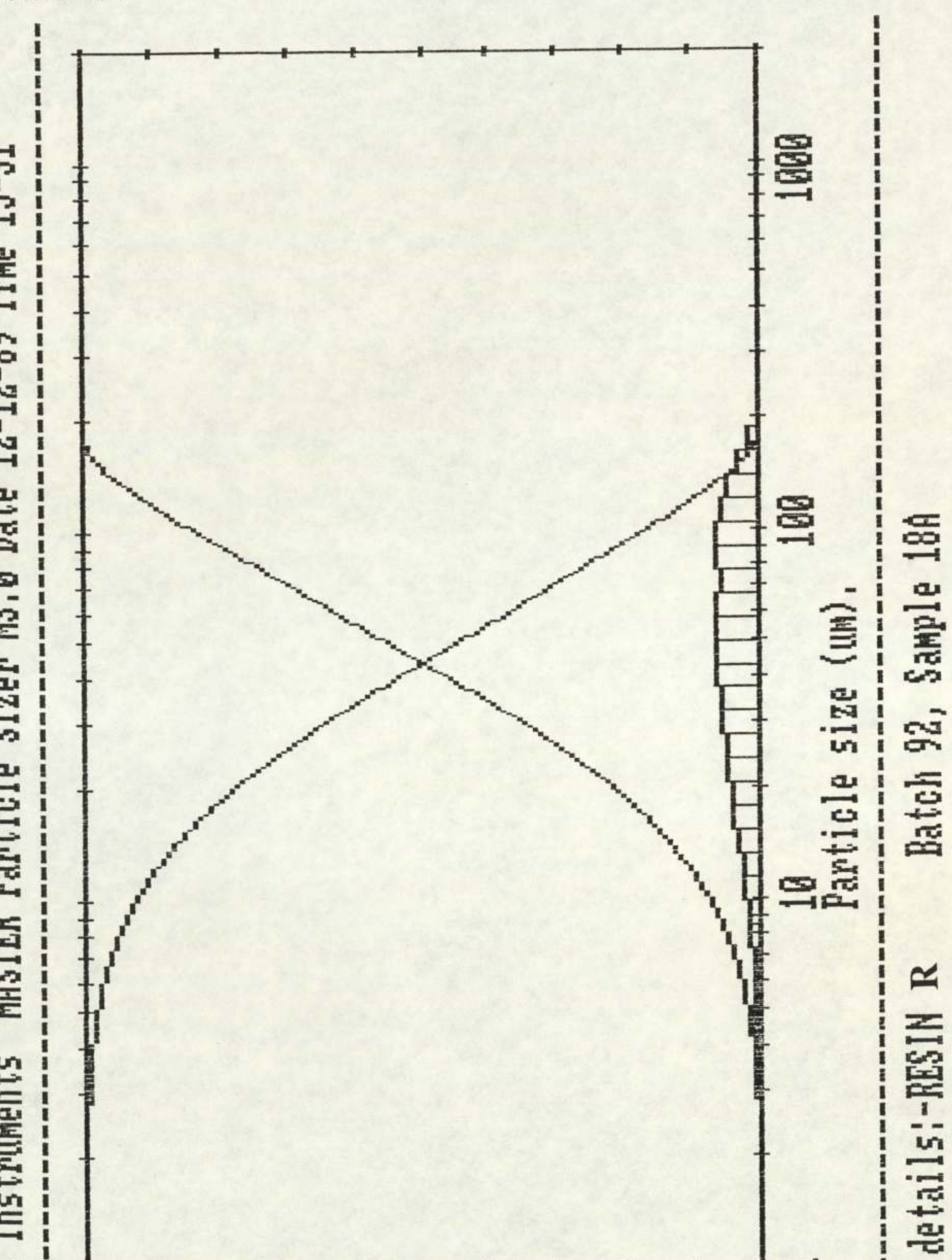


FIGURE 3a.2


Malvern Instruments MASTER Particle Sizer M3.0 Date 12-12-89 Time 15-31
100
%
50
0
1
10
100
1000
Particle size (um).
Sample details:-RESIN R Batch 92, Sample 18A

APPENDIX 3b

TABLE 1 : BATCH 92 SAMPLE IDENTIFICATIONS

Sample No.	*Time Into Reflux Cycle /hr*	*Sample No.*	*Time Into Reflux Cycle /hr*
10.A	0		
11.A	0.95	11.B	1.03
12.A	2	12.B	1.95
13.A	2.92	13.B	2.95
14.A	4.5	14.B	4.47
15.A	9.5	15.B	9.5
16.A	10.5	16.B	10.5
17.A	11.5	17.B	11.5
18.A	12.5	18.B	12.5

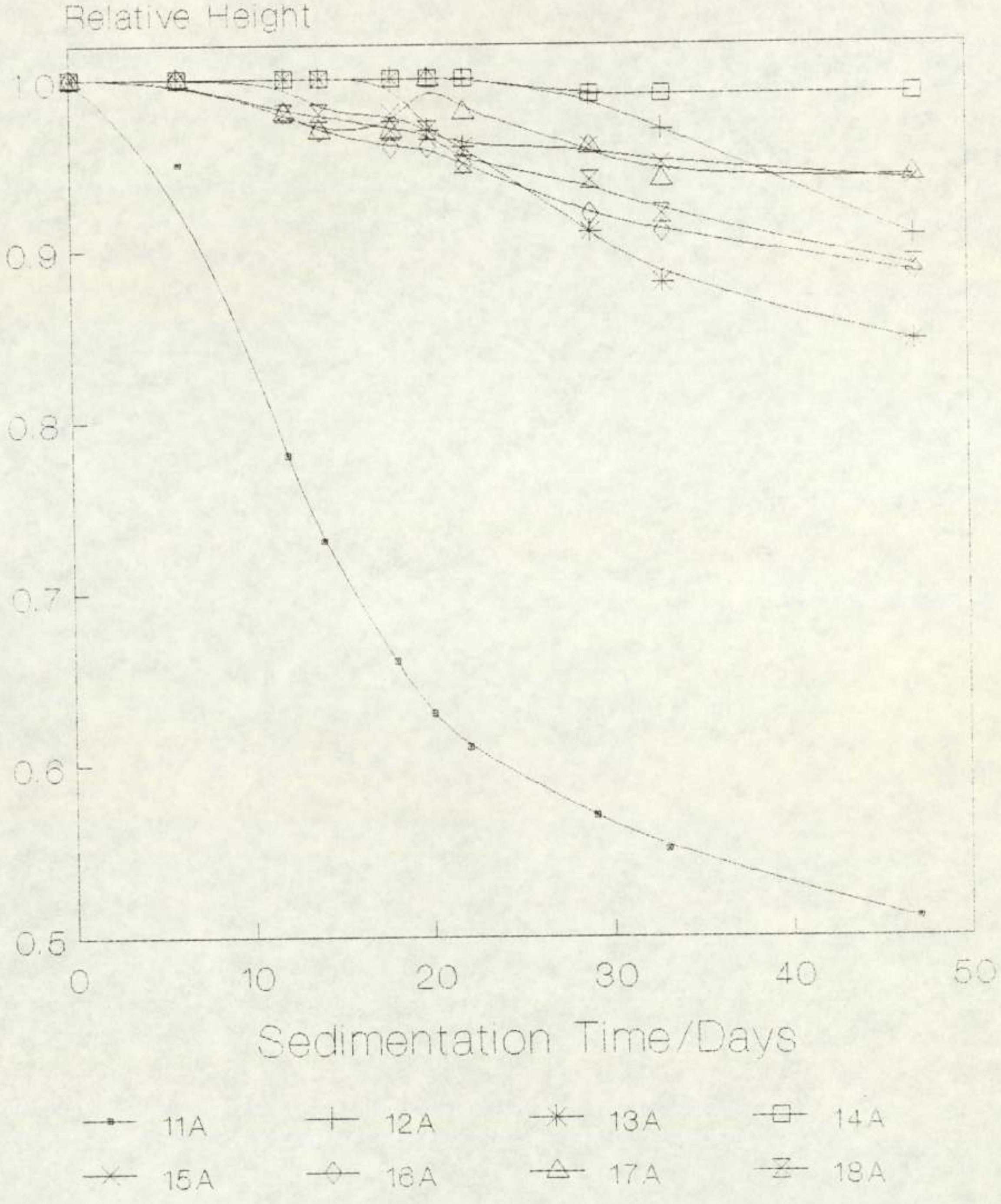
TABLE 2 : BATCH 95 SAMPLE IDENTIFICATIONS

Sample No.	*Time Into Reflux Cycle /hr*	*Sample No.*	*Time Into Reflux Cycle /hr*
20A	1	20B	1
21A	2	21B	2
22A	3	22B	3
23A	4	23B	4
24A	5	24B	5
25A	6	25B	6
26A	7	26B	7
27A	8	27B	8

SEDIMENTATION TEST RESULTS **APPENDIX 3b**

GRAPH 1

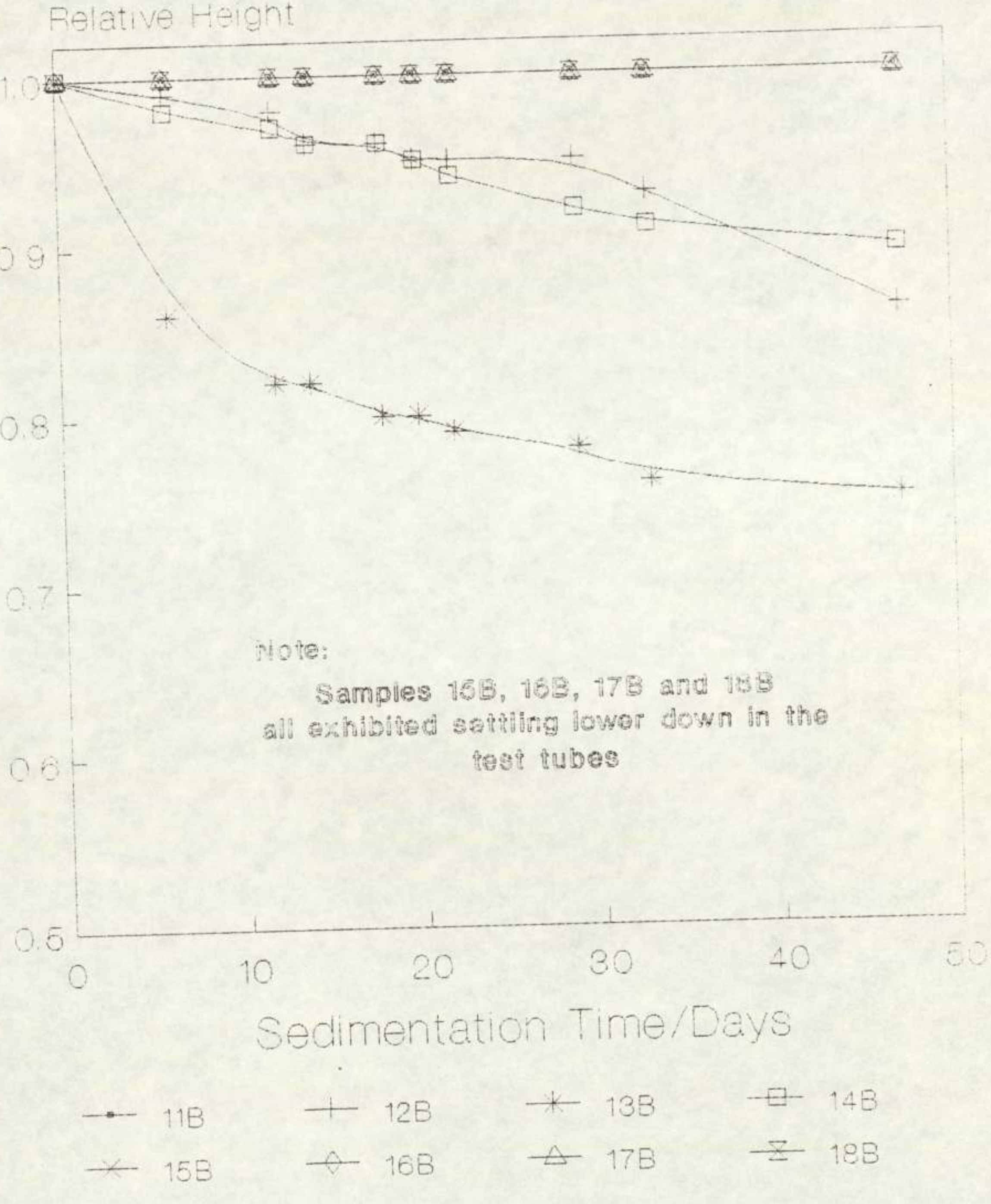
SEDIMENTATION
Resin R BATCH 92 - top of blender 2



APPENDIX 3b

GRAPH 2

SEDIMENTATION
Resin R BATCH 92 - bottom of blender 2



Note:

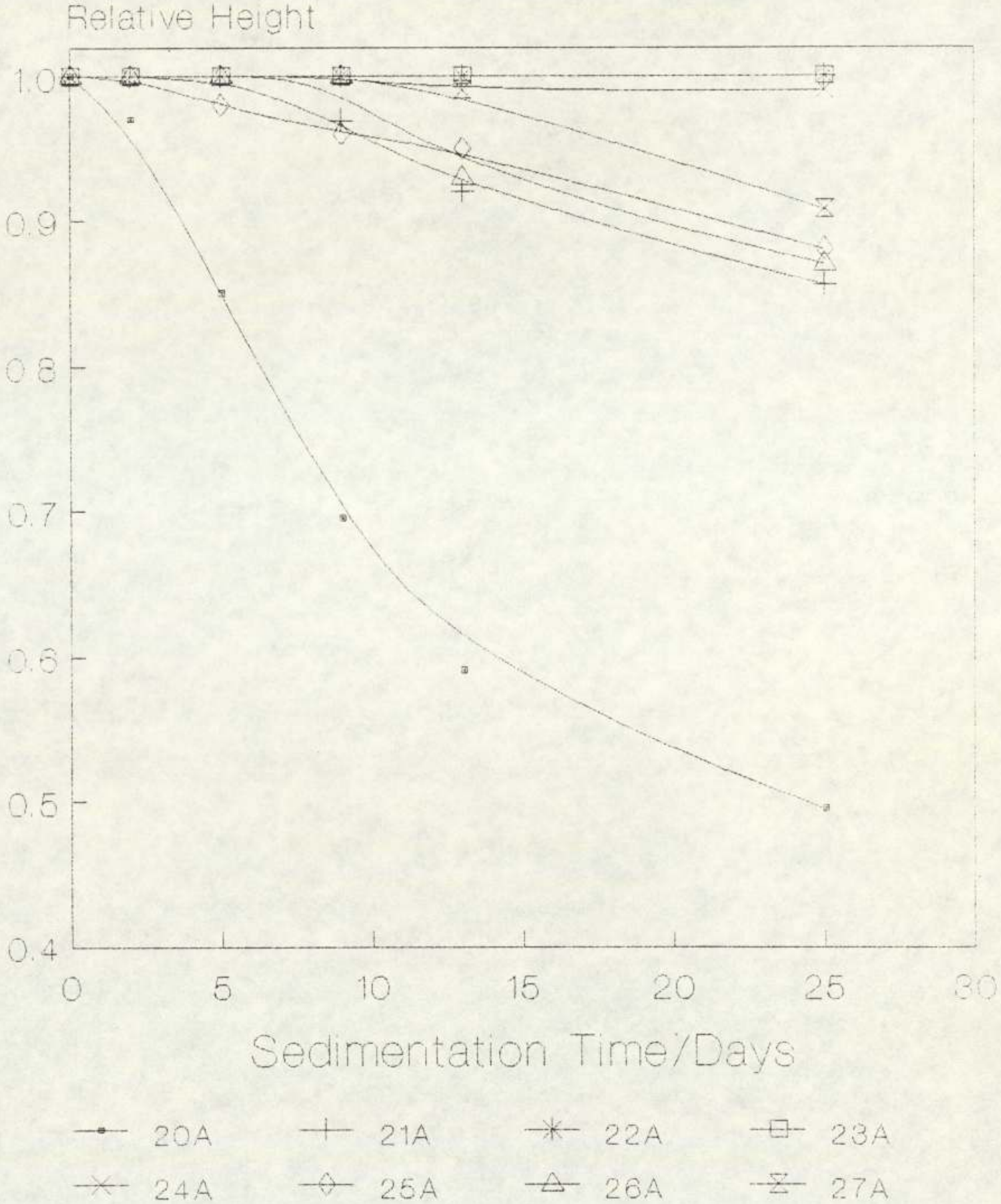
Samples 15B, 16B, 17B and 18B all exhibited settling lower down in the test tubes

APPENDIX 3b

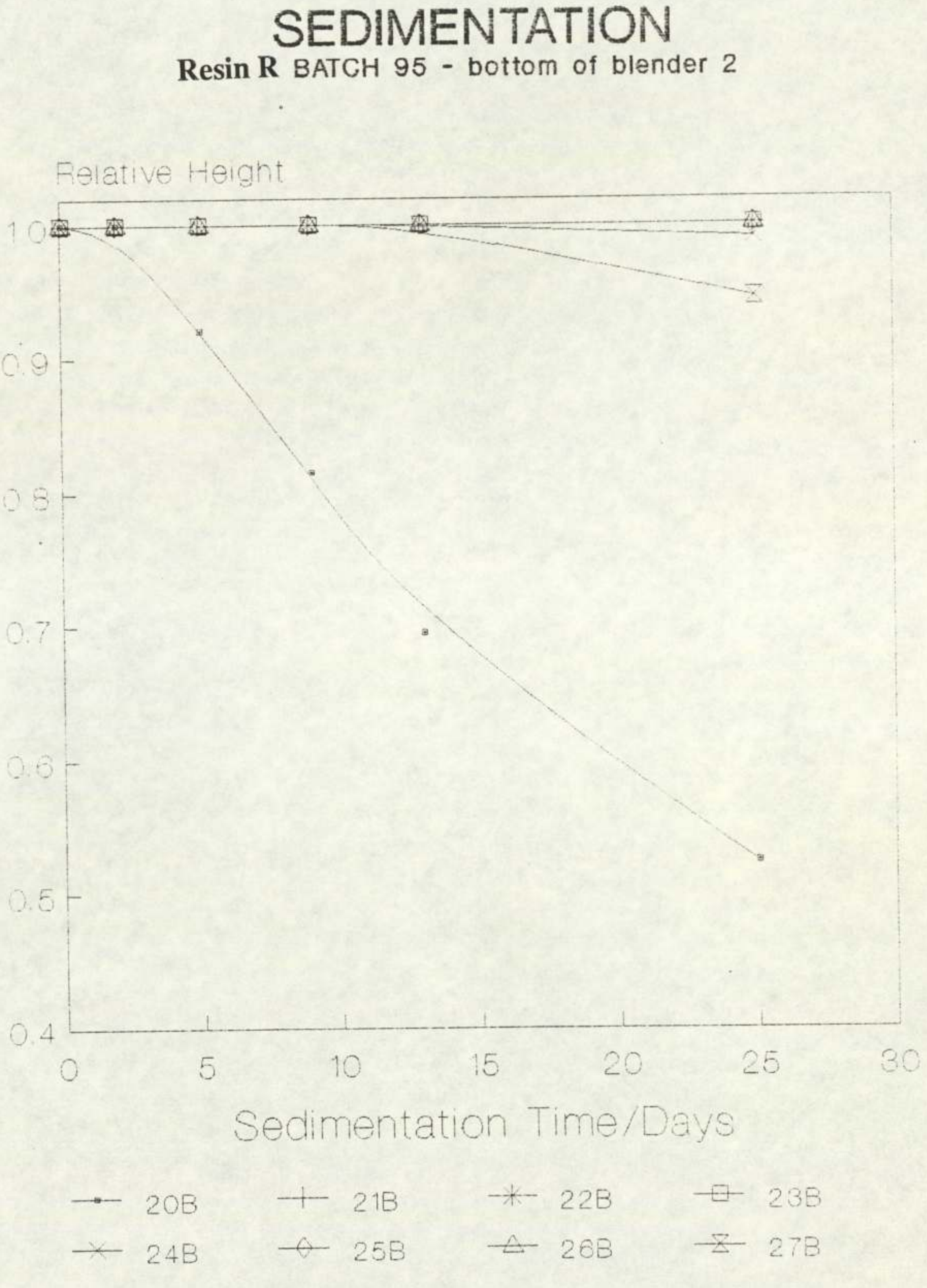
GRAPH 3

SEDIMENTATION

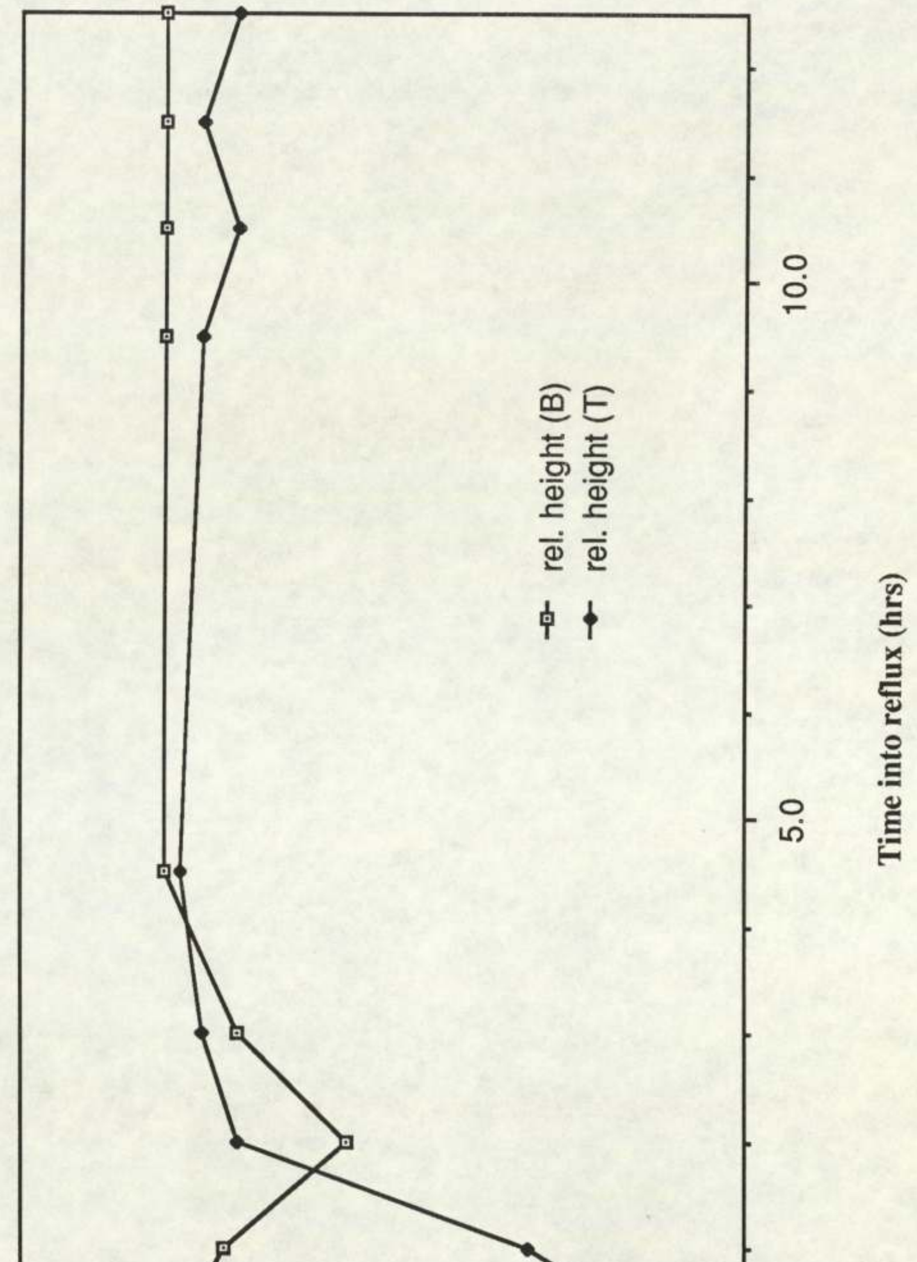
Resin R BATCH 95- top of blender 2



GRAPH 4

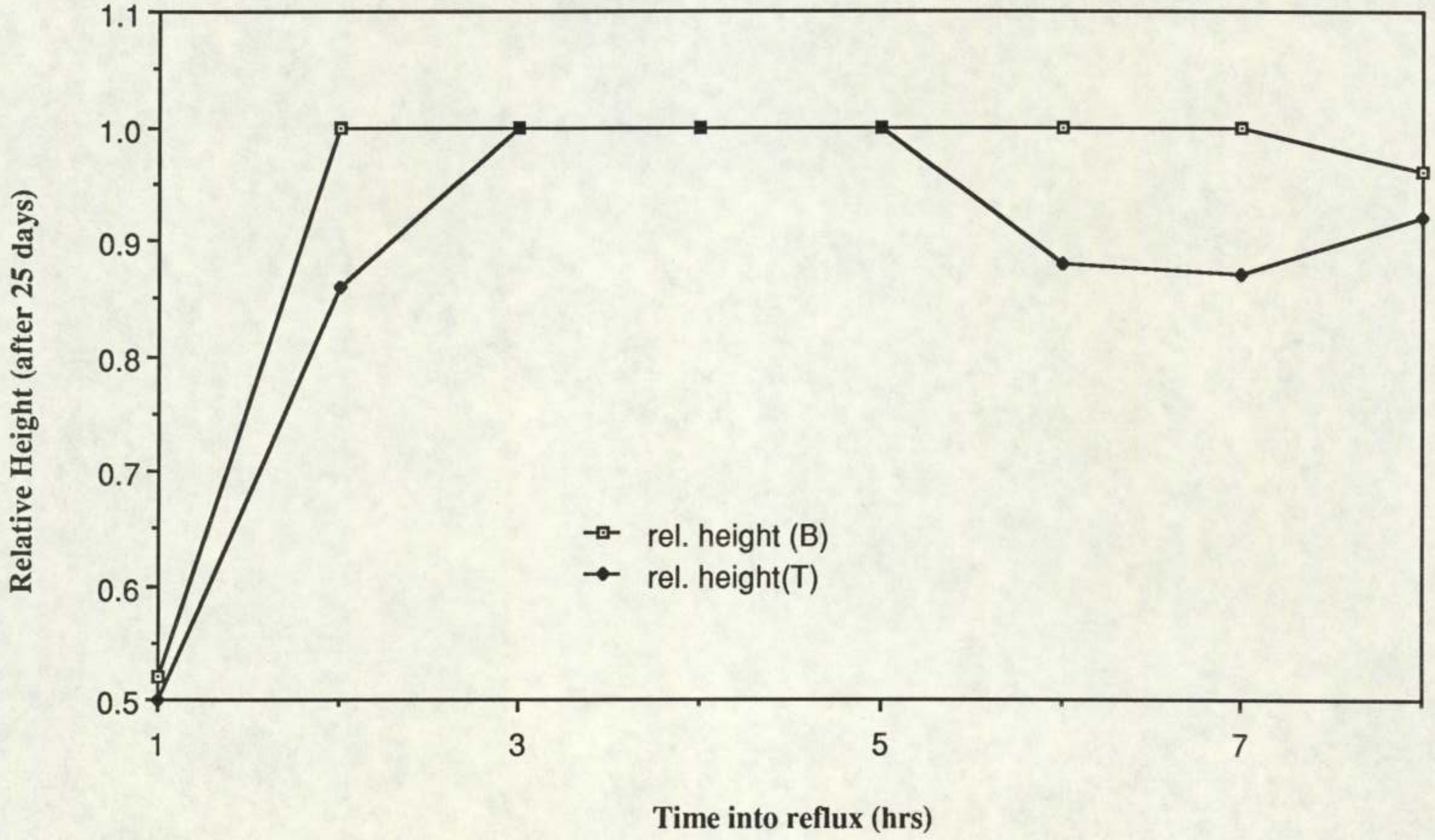

SEDIMENTATION
Resin R BATCH 95 - bottom of blender 2
Relative Height
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0
5
10
15
20
25
30
Sedimentation Time/Days
20B
21B
22B
23B
24B
25B
26B
27B

Graph 5; Sedimentation within Resin R/92



APPENDIX 3b

Graph 6; Sedimentation within Resin R/95



APPENDIX 3c

PARTICLE SIZE MEASUREMENT BY LASER DIFFRACTION

1 Equipment

The Malvern Particle Size Analyser comprises mainly of a laser light source, a lens and a detector with 31 concentric ring elements. A stirred cell is provided for analysis of solid particles suspended in a liquid medium, and a transparent tower is used for sprays from atomisers and nozzles. An IBM-PC compatible desk top computer is linked to the unit to run the software and produce result printouts via a printer. The basic equipment is shown in figure 1.

2 Principles of Operation

On passing a parallel beam of monochromatic, coherent light through a sample medium, the resultant illumination of suspended particles will cause a diffraction pattern to be superimposed on the geometric image. The pattern will be large compared to the image. A Fourier Transform Lens placed after the sample will cause undiffracted light to be focused to a point, with the diffracted light forming a ring around the central spot. The diffraction pattern caused by a specific particle is constant at any distance from the lens, no matter where in the illuminating beam it passes. The "far field" diffraction pattern that is produced is known as the Fraunhoffer Diffraction Pattern. The light distribution appears as a series of alternating light and dark concentric rings. The diameter of the pattern is inversely proportional to the particle diameter. The presence of several particles will produce a summed light distribution from which it is possible to separate the data to obtain the particle size distribution.

Mathematical models suitable for the sample are employed by the computer software, associated with the instrument, to fit the data. Two models which may be used in the analysis of solid particles are the "Independent" and "Log Normal" models. The Log Normal model was originally developed for the products of comminution and is now widely accepted for all such particles from industrial processes. The function defines the distribution to be normal and the logarithms of particle sizes. Two parameters, X and N (geometric mean and geometric standard deviation, respectively) are evaluated for each sample and the weight frequency is described by:

$$Ld = [1 / (n(N)*2)]* \exp [(1m(d) - 1n(X) / 2*(1n (N))^{2}]$$

where Ld indicates the relative frequency of size d.

This analysis assumes the particles to be spherical, so experimental inaccuracies may arise if their shape varies considerably from this.

APPENDIX 3c

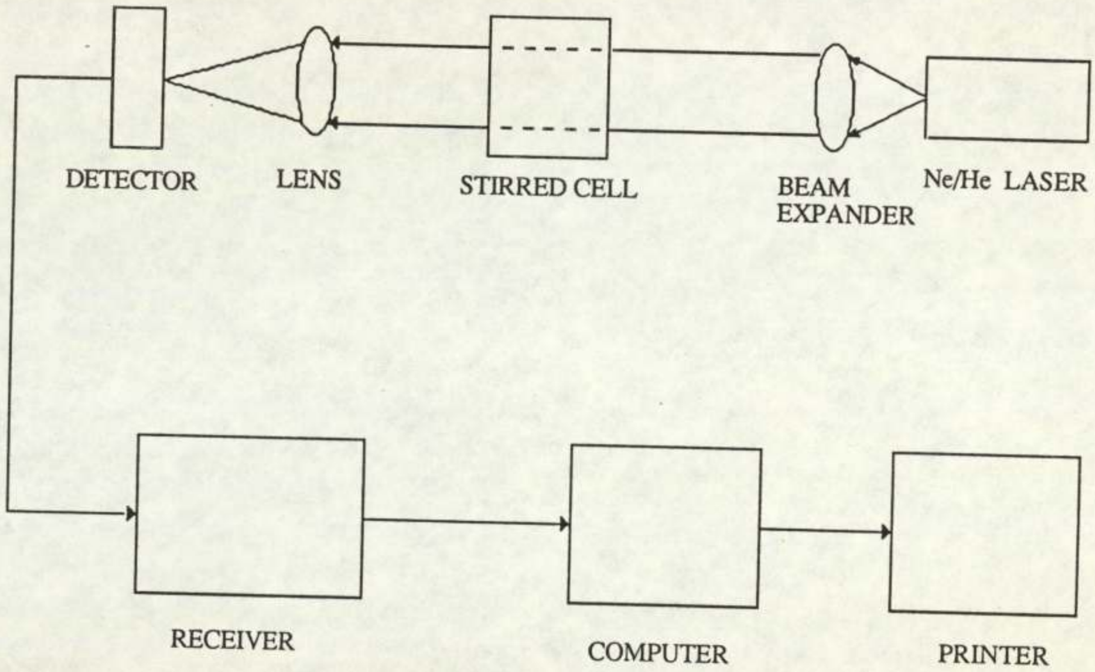


FIGURE 1; SCHEMATIC REPRESENTATION OF MALVERN PARTICLE SIZE ANALYSER

SECTION 4

CHAPTER 8

DETERMINATION OF THE UNREACTED GLYCOL CONTENT IN POLYESTER BASE RESINS AND ITS EFFECT ON FINAL RESIN PROPERTIES

8 DETERMINATION OF THE UNREACTED GLYCOL CONTENT IN POLYESTER BASE RESINS AND ITS EFFECT ON FINAL RESIN PROPERTIES

8.1 Introduction

For a number of years there has been some speculation as to the amount of unreacted glycol contained in polyester base resins. The general consensus is that there are small amounts (thought to be less than one per cent of the initial glycol charge) of unreacted glycol in these resins. This may be true if a glycol adjustment is made towards the end of the production process, since there may not be enough time for all the glycol to react into the resin. The presence of unreacted glycol in BIP base resins may reduce as the number of resins manufactured using the partial condensers increases (see Chapter 6), ie the initial glycol charge is retained, thus eliminating in-process glycol adjustments.

Glycol is known to be a thixotropic enhancer, ie small additions of glycol to a blended resin, before the aerosil is charged, will increase the thixotropy of the resin (see section 7.3.1). Therefore, any variation in the unreacted glycol content of the base resin will affect the thixotropy of the system. The presence of unreacted glycol may also have an effect on other properties of the resin, such as water resistance and pigment separation. It is known that higher levels of unreacted glycol will reduce water resistance and increase pigment separation within the resin:

eg: (i) Unreacted glycol is capable of hydrogen bonding with water and as a result the water resistance of the resin is reduced. This is particularly important if the resin is to be used to manufacture a boat hull or a bath tub.

(ii) Many resins are pigmented by customers to yield the desired colour, ie a bathroom manufacturer will require many different colour suites. The presence of unreacted glycol in the resin may result in pigment separation, giving a "streaky" appearance to the product.

It was the intention of this project to develop a method for the extraction, detection and analysis of unreacted glycol in polyester base resins. If successful, the new method(s) will be used to monitor batch to batch variation in unreacted glycol content and its subsequent effect on thixotropy, water resistance and pigment separation.

8.2 Experimental Procedure

Methods were required to extract, detect the presence of, and analyse unreacted glycol in base polyester resins. As such, the experimental work was divided into two main categories:-

(i) detection and analysis
(ii) extraction.

8.2.1 Glycol Analysis using Gas Chromatography

Gas chromatography was chosen to detect and analyse unreacted glycol, since the equipment was readily available at the University and previous work had evaluated this technique for such an application. (However, this was later proved to be of no use as the recommended column did not provide adequate separation.) Due to the lack of data available, it was decided that the gas chromatograph should be set up from "scratch", ie by selecting a column and developing the appropriate conditions.

All the development work was carried out using a Pye Unicam 204 Gas Chromatograph.

8.2.1.1 Selection of a Column and Suitable Control Parameters

A review of technical literature[16] was carried out to determine what columns are available for the detection of glycols. (Particularly propylene and diethylene, ie the glycols used in the production of BIP polyesters.) The columns which were evaluated and the appropriate control parameters are summarised in Table 8.1.

Table 8.1: Summary of Column Type and Chromatographic Conditions used to Separate Propylene and Diethylene Glycol

	COLUMN TYPE			
Chromatographic Conditions	SE30	Apiezon-L	Carbowax 20M	Porapak PS
Injector Temp (°C)	250	250	250	250
Detector Temp (°C)	250	250	250	250
Column Temp (°C)	200	200	200	200
Temperature Prog:				Not used
Initial Temp (°C)	80	150	160	
Time (mins)	2	1	1	
Final Temp (°C)	200	200	200	
Time (mins)	5	2	7	
Gradient (°C/min)	32	32	32	
Flow Rate (mls/min)	30	30	30	30
Sample Size (µl)	3	3	3	3
Attenuation	16	16	16	16

Note: The results in Table 8.1 are the final chromatographic conditions established for the test performance of each column. To obtain these parameters many variations were examined.

Initial conditions were obtained from the manufacturers' specification and adjusted in relation to peak separation and/or retention time of propylene and diethylene glycol. The performance of each column in Table 8.1 is described below.

(i) SE 30

This is a polar column and it was hoped that the glycols would be separated by their difference in polarity. Separation was not achieved with this column, possibly as a result of interaction between the glycols (eg hydrogen bonding), that, under the varying conditions used, did not permit separation.

(ii) Apiezon-L

The difference in volatility was examined when separating the glycols with this column. The Apiezon-L column is slightly polar and should provide the necessary separation through the difference in boiling point:

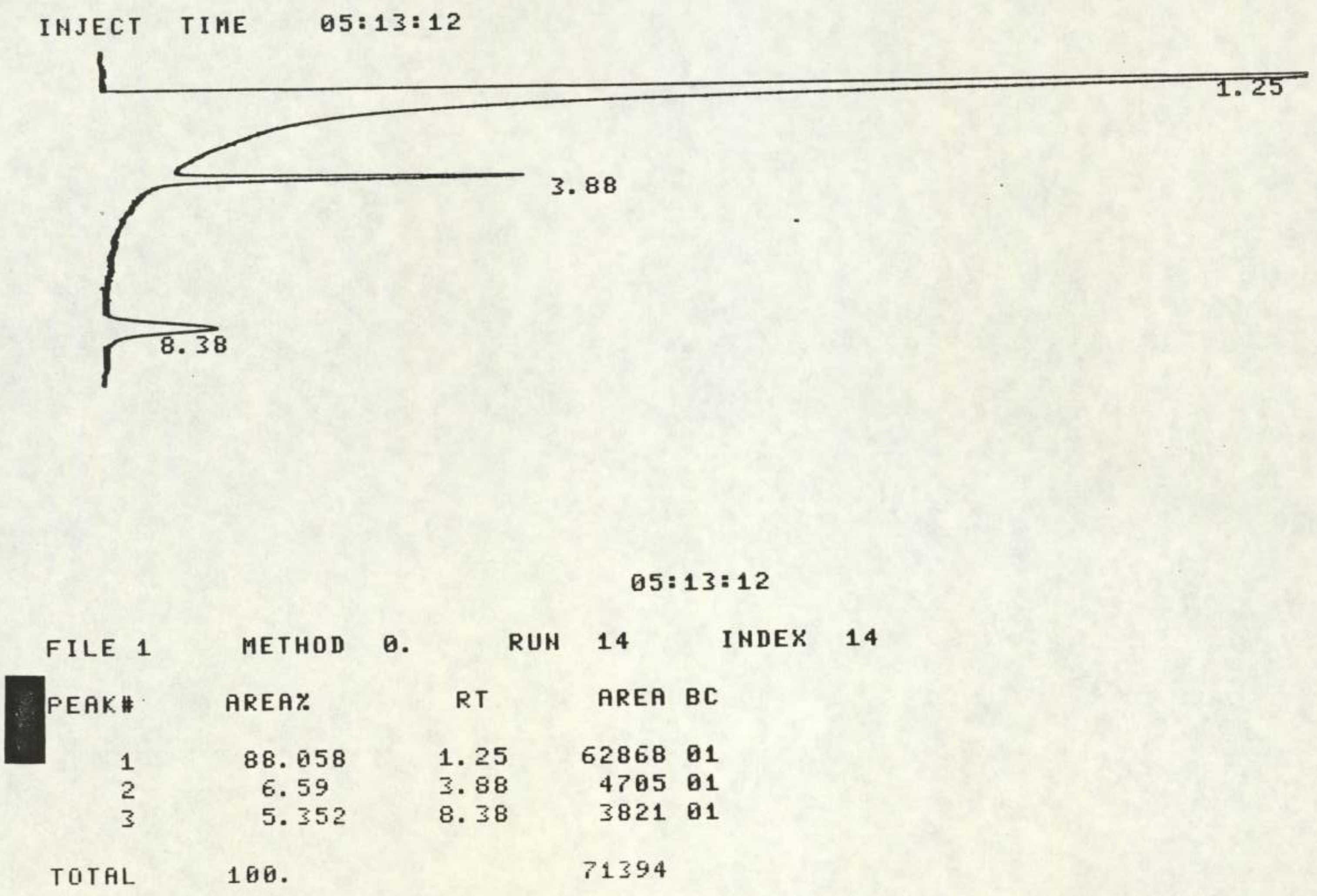
ie	propylene glycol	187.4°C
	diethylene glycol	245.0°C.

However, problems were encountered in detecting the diethylene glycol. The high boiling point of the diethylene glycol (245°C) is above the recommended operating temperature of the column (200°C), resulting in little/no detection of this material.

(iii) Carbowax 20M

Separation was achieved with this column (see figure 8.1). Propylene glycol appears with a retention time of 3.88 mins and diethylene glycol 8.38 mins. The large peak seen after 1.25 mins is water and was introduced to simulate analysis of samples from the solvent extraction technique, used to remove unreacted glycol from base resins (see section 8.2.2). Standard curves were required for both diethylene and propylene glycol so that unknown samples could be analysed. However, poor separation was observed when setting up the standard curves. It was suspected that the packing had become contaminated and the column could no longer be used.

FIGURE 8.1



```
INJECT  TIME    05:13:12

                              05:13:12

FILE 1      METHOD  0.      RUN  14     INDEX  14

PEAK#      AREA%        RT       AREA BC

    1        88.058     1.25    62868 01
    2         6.59      3.88     4705 01
    3         5.352     8.38     3821 01

TOTAL      100.                 71394
```

(iv) Porapak PS

The need for a new column prompted consultation with Jones Chromatrophy[16] (manufacturers of packed columns), who recommended the purchase of a Porapak PS column (a non-polar porous polymer) to separate the glycols. The chromatograph was set up with the control parameters used for the Carbowax 20M column and adjusted to achieve adequate separation, until eventually separation was obtained with the conditions recorded in Table 8.1. Analysis with this column is illustrated in the chromatogram of figure 8.2. The components can be identified by their retention times (see Table 8.2).

Table 8.2: Retention Times

Component	Retention Time (mins)
Propan-2-ol	1.1 - 1.6
Propylene Glycol	3.1 - 4.2
Diethylene Glycol	9.8 - 12.7

Propan-2-ol is an internal standard (see section 8.2.1.2) used in the preparation of standard curves (see section 8.2.1.3).

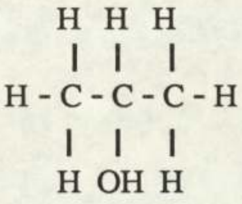
8.2.1.2 Selection of an Internal Standard

An internal standard is required to account for any discrepancies when injecting samples, ie a known amount of internal standard is added to each sample and the peak area recorded. This value is compared to the peak area obtained from a standard addition. If there is a difference between the two, the peak area of the internal standard in the unknown will be corrected. The peak areas of other components in the sample will be adjusted in the same proportion.

eg: peak area of the internal standard in the unknown is lower than the predetermined value. Therefore, the peak areas of the internal standard and other components in the unknown will require the same reduction.

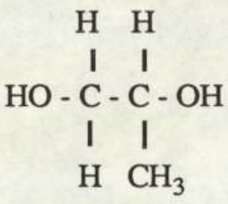
Propan-2-ol was selected as the internal standard, due to its similarity in chemical structure to the glycols.

ie:



$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{OH} & & \mathrm{H} & & \end{array}$$

Propan-2-ol



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & \\ \mathrm{HO} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{OH} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{CH_3} & & \end{array}$$

Propylene Glycol

$HOCH_2CH_2 - O - CH_2CH_2OH$

Diethylene Glycol

It is a volatile substance (boiling point 81°C - 83°C) and is therefore suitable for gas chromatography. The volatility means that the peak appears first on the chromatogram (see section 8.2.1.1 (ii) for glycol volatilities), thus making Propan-2-ol an ideal internal standard.

8.2.1.3 Preparation of Standard Curves

The separation achieved by the Porapak PS column resulted in its use for the preparation of standard curves. When established, the standard curves may be used to identify the unreacted glycol content in polyester base resins, provided a suitable extraction method is available (see section 8.2.2.).

Standard curves for propylene (see Table 8.3 and figure 8.3) and diethylene glycol (see Table 8.4 and figure 8.4) were produced over the range 0.5 mass % glycol to 10 mass % glycol.

Table 8.3: Propylene Glycol
- *see Figure 8.3.*

Sample	Area Propylene Glycol	Propan-2-ol		Mass % Propylene Glycol	Mass % Propan -2-ol	$\frac{\text{Area PG}}{\text{Corrected Area P-2-ol}}$
		Area	*Corrected Area			
1	458	5265	5297	0.542	4.97	0.086
2	1196	5373	5330	1.025	5.04	0.224
3	2010	5083	5083	2.150	5.00	0.395
4	5133	5357	5325	5.210	5.03	0.964
5	6593	3563	3549	10.01	5.02	1.860

Area = Peak Area

$$\text{* Corrected Area} = \frac{5.0}{\text{mass \% propan-2-ol used.}} \times \text{Peak Area}$$

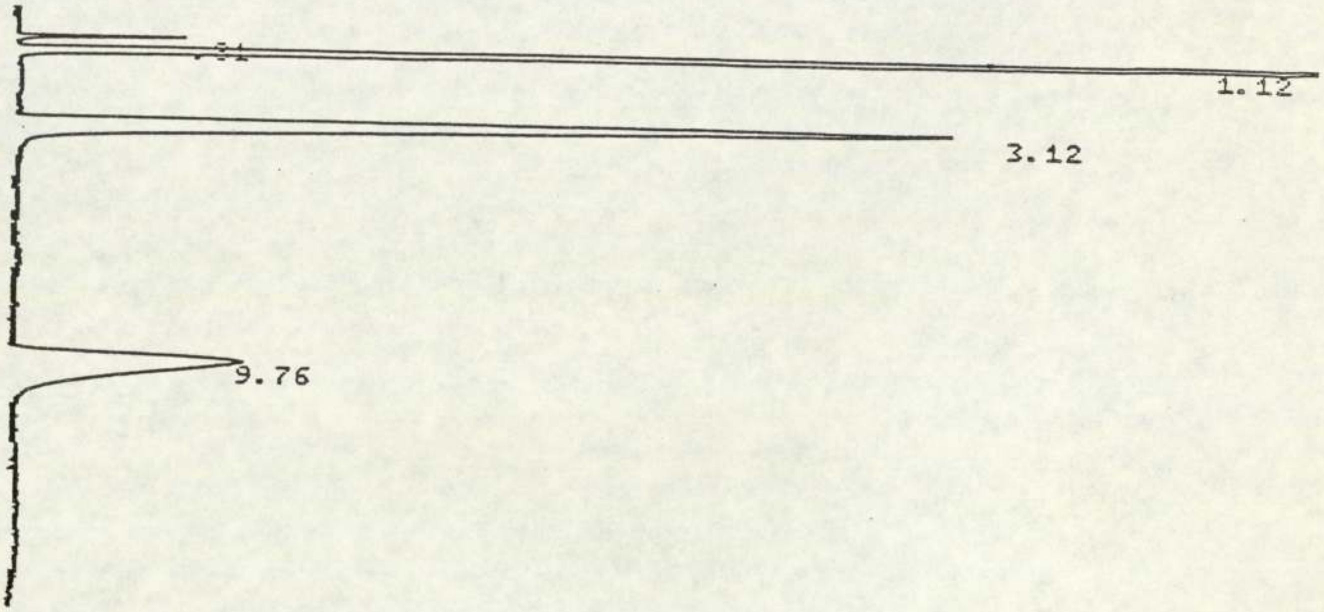
Since 5 mass % Propan-2-ol was not used in each standard, the areas were adjusted accordingly.

Table 8.4: Diethylene Glycol
- *see Figure 8.4.*

Sample	Area Propylene Glycol	Propan-2-ol		Mass % Diethylene Glycol	Mass % Propan -2-ol	$\frac{\text{Area DEG}}{\text{Corrected Area P-2-ol}}$
		Area	*Corrected Area			
1	582	3576	3540	0.500	5.05	0.164
2	1390	4893	4903	1.12	4.99	0.283
3	2201	4801	4772	2.08	5.03	0.461
4	4484	4853	4786	5.07	5.07	0.924
5	8861	5004	4964	10.08	5.04	1.79

FIGURE 8.2

```
JECT  TIME    02:03:17
```



```
                              02:03:17
 LE 1      METHOD  0.      RUN   1      INDEX   1

PEAK#      AREA%         RT      AREA BC



   1        1.556       0.81       866 01
   2       36.579       1.12     20363 01
   3       39.795       3.12     22153 01



   4       22.07        9.76     12286 01

TOTAL     100.                   55668
```

FIGURE 8.3

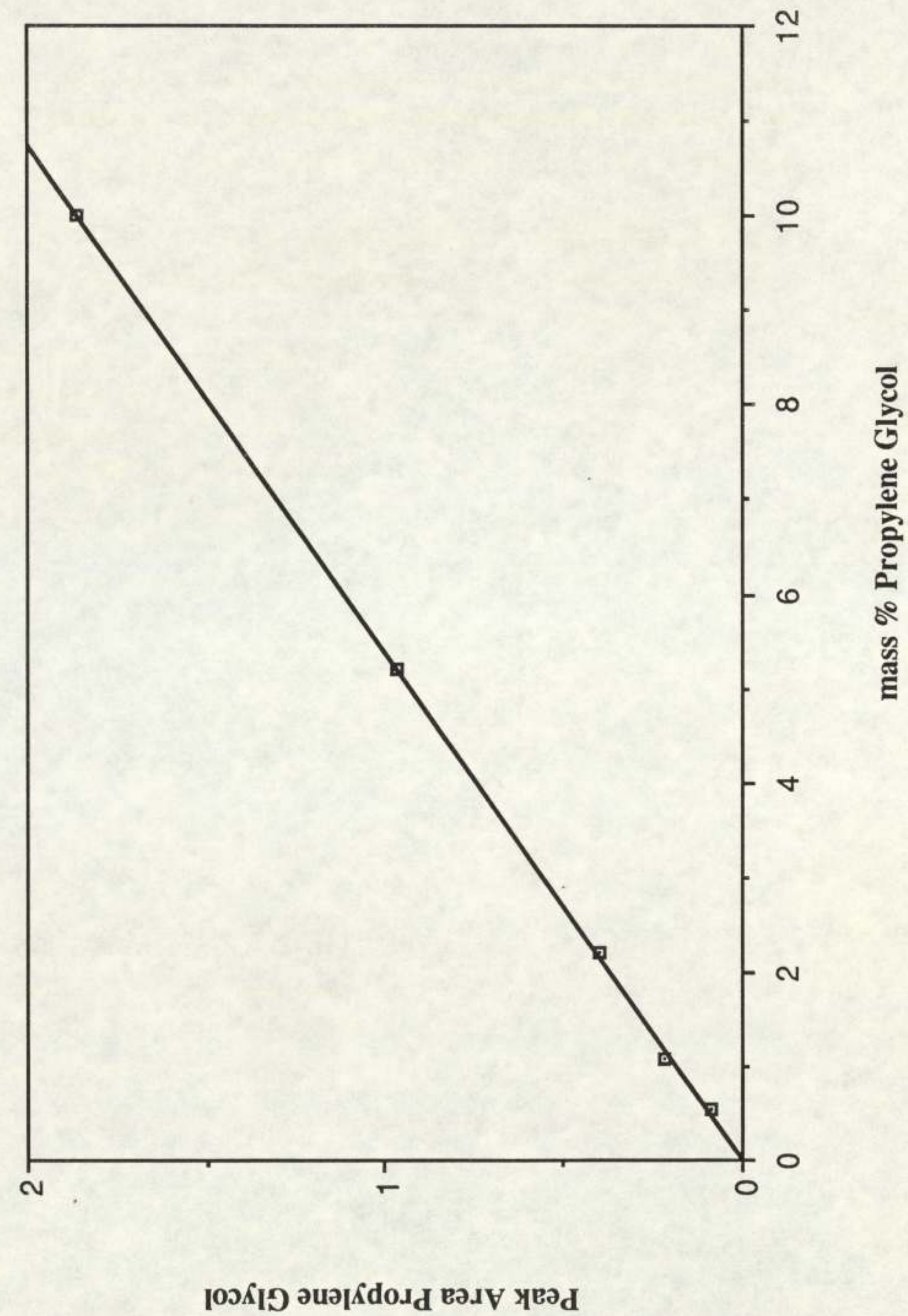


Figure 8.3; Calibration Curve Propylene Glycol

FIGURE 8.4

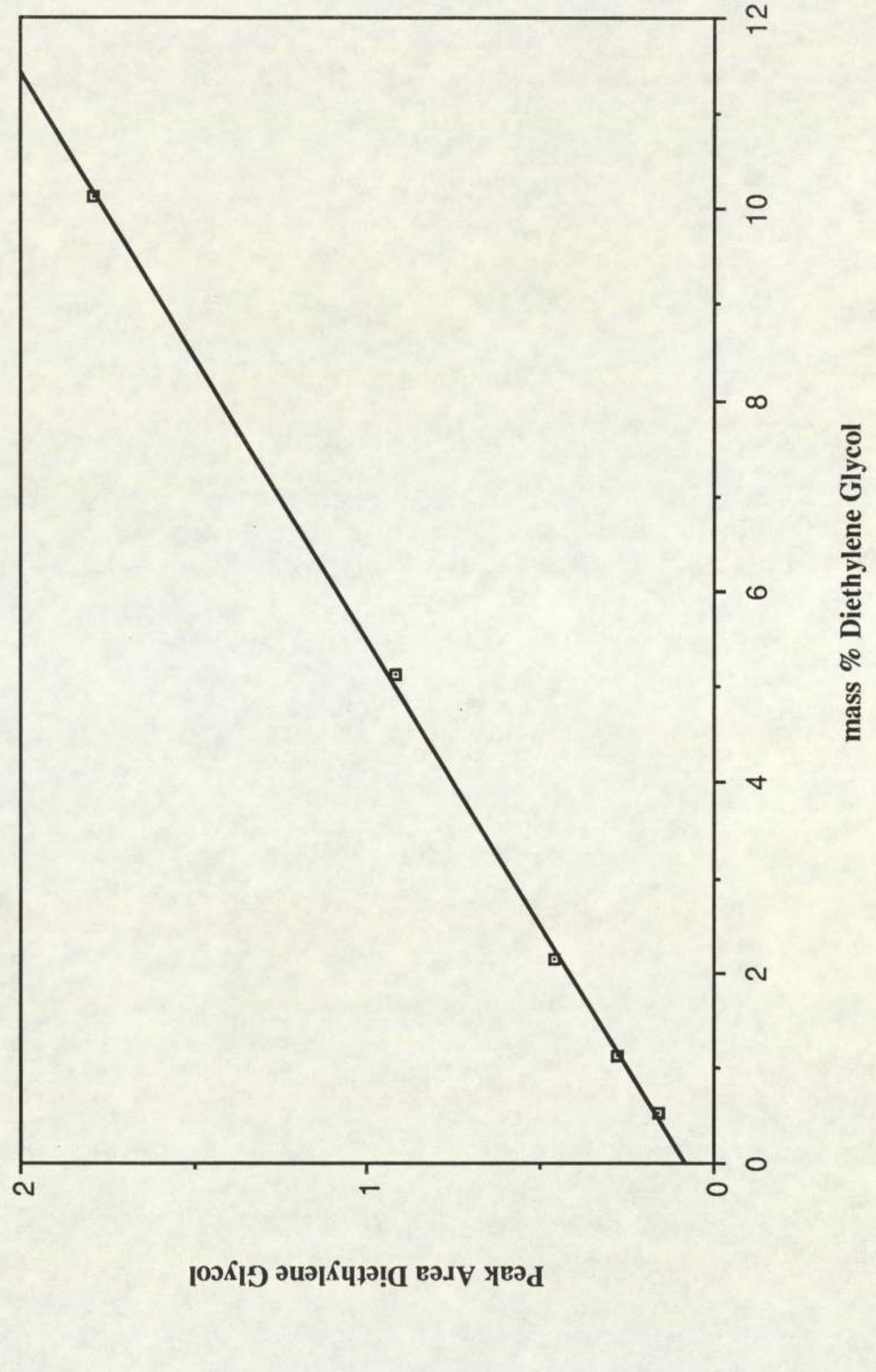


Figure 8.4; Calibration Curve Diethylene Glycol

The standard curves were prepared with glycols obtained from the polyester plant and not AnalaR grade reagents. This is reflected in the chromatogram with the presence of an impurity, retention time 0.81 mins (see figure 8.2).

The propylene glycol standard curve (see figure 8.3) shows good analysis of samples over the range studied (ie 0.5 mass % to 10. mass % propylene glycol), and is in fact a good straight line through the origin. The diethylene glycol standard curve (see figure 8.4) appears to show a reasonable agreement over the range studied. However, the line does not bisect the origin, and a sample containing O mass % diethylene glycol would be expected to produce a peak area ratio, diethylene glycol : propan-2-ol, of 0.75. Therefore, samples containing trace amounts of diethylene glycol (ie less than 0.1 mass %) would not be detected. Repetition of the standard curves will be required using AnalaR grade reagents to eliminate impurities from the traces and improve the accuracy of analysis. However, it is felt at this stage that the Porapak PS column has been successfully commissioned by achieving good separation of the glycol components over the 0.5 mass % to 10 mass % range. When a suitable extraction technique has been developed (see section 8.2.2), the Porapak PS column and the corresponding conditions in Table 8.1 will be used to detect and analyse the presence of unreacted glycol in polyester base resins.

8.2.2 Extraction of Unreacted Glycol from Polyester Base Resins

Two methods were selected to extract unreacted glycol from the base resin:-

(i) Solvent Extraction
(ii) Vacuum Distillation.

Time constraints did not permit examination of the vacuum distillation method. However, there is no reason to prevent development of this technique at a later date.

8.2.2.1 Solvent Extraction

All the experimental work was carried out with a batch of resin AM manufactured on reactor 7. At the time of examination reactor 7 suffered the greatest glycol losses, since the partial condenser[6] had not been installed. The result was that many glycol adjustments were required throughout the process, thus increasing the probability that unreacted glycol may be present in the resin.

The following method was developed to extract unreacted glycol:-

(i) Weigh out 100 g of resin.
(ii) Extract with 3 x 100 mls of water.
(iii) Combine the extracts and filter to remove any resin carried over.
(iv) Concentrate the sample by removing the water.
(v) Cool the sample in a refrigerator and filter to remove any oligomers which may have been extracted. Some oligomers (ie short chain polyesters) may be small enough to represent a glycol molecule and will therefore be extracted.
(vi) Analyse the samples by gas chromatography (see section 8.2.1).

A solvent extraction method was examined in the hope of providing a quick, simple test. Water was chosen as the solvent to extract unreacted glycol from the resin. The formation of hydrogen bonds between unreacted glycol and water should be sufficient to extract the glycol from the resin. However, some glycol may remain due to the formation of hydrogen bonds between the unreacted glycol and terminal end groups of the polyester chains,. How much glycol remains in the resin can be determined by measuring the efficiency of extraction, eg known glycol additions made to the resin, extracted with water and analysed by gas chromatography. The percentage glycol regained will provide a measure of the efficiency of extraction.

A resin sample containing a glycol addition was extracted and analysed to determine whether or not the solvent extraction and gas chromatographic techniques were acceptable. Both propylene and diethylene glycol were observed in the chromatogram (see figure 8.1), proving that both techniques were suitable for the detection of unreacted glycol in polyester base resins. Further work is required to measure the efficiency of extraction and if necessary improve the analytical procedure.

Vacuum distillation may be the preferred technique since smaller amounts of unreacted glycol may be extracted. Analysis (of samples from the vacuum distillation procedure) by gas chromatography will become easier, as water is no longer required, thus eliminating its peak from the chromatogram, ie the number of components in the trace is reduced.

When a suitable extraction method has been developed, the relationship between unreacted glycol and final resin properties will require some attention.

8.3 Conclusions

(i) The Porapak PS column can separate propylene and diethylene glycol.

(ii) The column was successfully commissioned with the production of standard curves for both diethylene and propylene glycol over the 0.5 mass % to 10 mass % range.

(iii) A solvent extraction method has been developed which is capable of extracting unreacted glycol from polyester base resins. More work is required before introducing the technique, eg measure the efficiency of extraction.

8.4 Recommendation

(i) Use gas chromatography with a Porapak PS column to detect and analyse propylene and diethylene glycol.

8.5 Further Work

(i) Measure the efficiency of the solvent extraction technique.

(ii) Explore the possibility of vacuum distillation to extract unreacted glycol from polyester base resins.

(iii) When a suitable extraction method has been developed, examine the relationship between unreacted glycol and final resin properties, ie thixotropy, water resistance and pigment separation.

8.6 References

16 "Packed Columns and Materials for Packed Columns"; Jones Chromatography, Tir-y-berth Industrial Estate, New Road, Hengoed, Mid-Glamorgan, CF8 8AU.