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**INTUMESCENT FORMULATIONS INCORPORATING
MELAMINE PHOSPHATE**

**PAULA THERESA ANNE KNOTT
DOCTOR OF PHILOSOPHY**

**THE UNIVERSITY OF ASTON IN BIRMINGHAM
MARCH 1988**

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The University of Aston in Birmingham

Intumescent Formulations Incorporating Melamine Phosphate

Paula Theresa Anne Knott

Doctor of Philosophy

1988

Summary

The available fire test rig developed by M.Kay(10) was recommissioned to facilitate the application of new Technology. The rig was modified to enable continuous visual recording of fire tests by means of a sophisticated VHS video system, and continual sampling of rig temperatures by computer. The tape recording of Fire Tests proved very successful in allowing repeated and detailed examination of any test.

Production of Melamine Phosphate was scaled up from the small scale laboratory method to a 900 litres pilot plant. Operating problems were identified and possible solutions are discussed for commercial scale production methods. The product was evaluated by fire testing, chemical analysis and particle size, shape and size distribution.

Different cure regimes for the epoxy matrix of the finished mastic were investigated. It was found that an ambient temperature cure was acceptable, and that small surface areas of application did not require surface priming, but it is considered that larger areas would benefit from substrate priming. Weathering tests show that little Melamine Phosphate was leached from the cured mastic, and samples performed satisfactorily during fire test.

Mastic preparations to improve handliability, applicability and fire resistance were formulated and tested. It was found that standard formulations, modified by the incorporation of thixotropic agents, expanding graphite, selected fillers and an organic solvent resulted in a better uncured mastic which had improved fire resistance after curing. Mastic formulations for different types of fire are proposed for further investigation.

KEYWORDS: Intumescent
Fire Retardant
Melamine Phosphate
Thixotropic

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Finally I want to thank my unfailing husband Peter, without whom I would never have completed this thesis.

DEDICATION

I wish to dedicate this work to my husband, Peter, who has always helped me through the most difficult times in my life.

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CHAPTER ONE
INTRODUCTION

CHAPTER ONE

INTRODUCTION

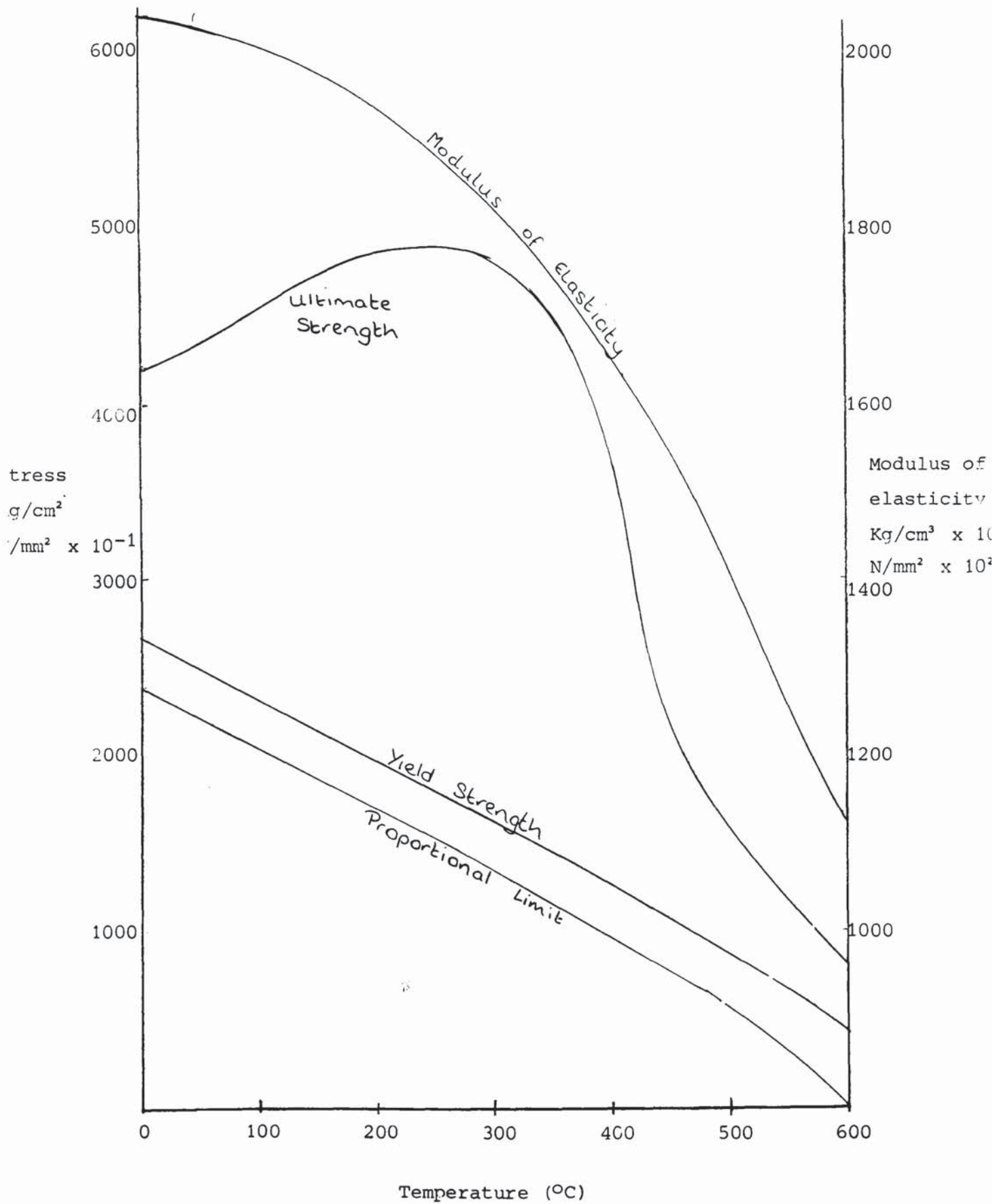
In 1977 £233.7 million [1] was lost due to industrial fires, by 1984 [2] this had increased to £520 million despite increasing amounts spent on fire protection; any means of improving the performance and reducing the cost of such protection must merit consideration.

There are two overall fire protection strategies, that of active fire prevention by use of sprinkler systems and similar measures in public buildings, and secondly passive fire protection which is the provision of intrinsic fire retardant properties by suitable pretreatment of the substrate. The two approaches closely complement each other.

In industry the main area to be protected is the structural steelwork which will not oxidise at temperatures normally encountered in fires, but above a certain critical temperature (550 °C for most mild steel) [3] will rapidly lose most of its strength which may lead to collapse of structural members. By reducing the rate at which this critical temperature is reached, more time is allowed for the fire to be extinguished. Figure 1.1 shows how the strength of steel varies with temperature, it may be seen that with temperatures above 300-350°C steel rapidly loses its strength. The designation of critical temperature as 'that beyond which the steel work will no longer be able to support its load' is somewhat arbitrary, being dependent upon the design safety factor incorporated; a working load of 0.55 yield strength is normally assumed [4]. Using Figure 1.1, the critical temperature can be seen to be 550°C. Oxidation in a fire may cause disintegration at temperatures well below the theoretical critical temperature of metal.

Figure 1.1

Strength and deformation characteristics of a structural mild steel as a function of temperature



It is not only steelwork that needs protection from fire, many other industrial plant items require some form of protection, for example pipework, tanks containing flammable liquids, plastic/synthetic pieces of equipment etc. The three main objectives of passive fire protection may be discerned:

- (a) The reduction of flame spread and spontaneous ignition of combustible material by the maintenance of a suitably low substrate temperature, normally by the use of fire retardent coatings. A special case of this is the protection of tankers and containers holding flammable and heat sensitive chemicals.
- (b) Structural fire protection, the object of which is the avoidance of collapse of structural members due to loss of strength caused by excessive rise in temperature.
- (c) The rendering of normally flammable materials, such as wood and some plastics flame retardant by the addition of suitable chemicals. It must be noted that it is the fumes rather than the flames themselves that are the greater hazard to human life, so the additives should also aim to be effective in smoke suppression.

Structural fire protection may be defined as the application of structural design features which retard the spread of flame and the rate at which the effects of exposure to fire are felt by a building. A reduction in the rate of rise of temperature is the normal criterion required of such a design feature, which may take the form of a coating onto the structural members, or the use of certain materials such as massive steel sections of high thermal capacity and configurations which reduce the rate of rise of temperature below that which would otherwise have been expected. With existing structures surface coatings may be used.

There are two basic categories of fire retardant coatings, those that act as inert insulators due to their low thermal conductivity, and those that undergo a chemical reaction when exposed to the fire. Concrete, expanded vermiculite, gypsum, plaster, mineral earths, mineral fibres and vitreous coatings belong to the former category, and if not physically damaged by the fire remain effective against further fires. The latter category includes intumescent and subliming coatings.

Lightweight vermiculite concrete, mineral fibre based coatings and intumescent coatings are suitable for the protection of structural steel work against fires, in many cases these may be fibre reinforced or utilise a compound coating, for example an overcoating of intumescent material on a concrete subcoat. The main disadvantages of vermiculite concrete are, firstly the thickness of coating required, for a fixed period of protection, hence the weight per unit surface area, and secondly the problem of spalling - the explosive ejection of particles of concrete when exposed to high temperatures in a fire. Mineral fibre overcomes the weight per unit surface area, but here the problem lies in the potential hazard in preparation. Both the above cases have a relatively low cost compared to intumescent coatings, but the latter only requires a thin coat, 3-8mm. The major shortcomings with intumescent mastics are smoke production and lack of durability.

To fulfill their role effectively in a fire, fire retardent coatings must also be securely bonded onto their structures in such a way that detachment will not occur in a fire. In the case of external coatings they must exhibit reasonable weatherability, possibly under a variety of conditions, eg. industrial atmosphere, marine exposure, extreme temperatures and humidities. Active components must not be leached out as this would render the coating ineffective. Physical impact or shear resistance may be required, on mobile items such as tankers, low density and thinness of coating are other, often mutually exclusive factors to be considered.

1.1 Intumescent Coatings

Intumescent mastics are fire protective coatings which act sacrificially, foaming on exposure to fire, the foamed char produced gives limited protection to the substrate, and so allowing time to extinguish the fire before the collapse of the structure. By virtue of their expansion they can also act to block gaps through which fire could spread and are thus used on fire doors on the surfaces between frame and the door (intumescent tape is available for this and similar situations). A honeycomb mesh system intumescently coated can be installed in a ventilation duct so preventing fire travelling this way. An intumescent mastic is used on oil rigs and in chemical plants to seal round pipes passing through fire walls by blocking off the gap in the event of a fire. These characteristics have made intumescent coatings attractive also to the aerospace industry, the US National Aeronautics and Space Administration (NASA) is active in the development of these materials.

Nevertheless intumescent coatings do suffer several disadvantages, their high cost is a commercial one. The technical disadvantages are given below:

- (a) Many components traditionally used in intumescent coatings are partially water soluble, and being hydrophilic are leached from coatings by water. Thus they generally have inferior weathering characteristics. WF Moran and LC Kynas [5] describe a method of overcoming the problem of water sensitivity of many aqueous intumescent coatings by applying a solvent based top coat for protection, though it should be noted that adding a second non-intumescent coat to a coat of Intumescent paint may not reduce flame spread but, on the contrary may reduce intumescence. Many attempts have been made to modify or treat the components of the mastic to improve the weatherability, these will be detailed under the components section.
- (b) Intumescent paints do not behave well with respect to good paint characteristics,

such as can-stability, brushability, being aesthetically pleasing, and being available in a wide range of colours. They have very high loadings of the intumescent components which are not compatible with the characteristics expected of a well formulated paint. Hiding pigments, resinous binders, bacteriostats and fungicides, flow promoters, sag inhibitors must all be incorporated with the consideration that they must not be detrimental to the intumescent properties of the system. Undesirably high ion concentrations and corrosiveness may be problems in paints with acidic constituents.

- (c) A paint normally only forms a thin film. Even when foamed the density of char produced from such a typical paint film is sufficient to protect a substrate for only a few minutes. It was not until intumescent mastics were developed that intumescent coatings could compete with the established means of protecting structural steel work and other exterior edifices against fire.
- (d) Unlike materials such as concrete, intumescent materials are consumed by fire their action is sacrificial. Noxious gases are evolved, oxides of carbon, ammonia, hydrogen cyanide, and, where chlorinated media are used, hydrogen chloride. Smoke may also be evolved. These are obviously undesirable if people are in the vicinity of a fire and likely to be exposed to such fumes.
- (e) Nominal coating thickness may be in error by a considerable amount. The problem of ensuring accurate application of a coating to a stated thickness has been highlighted by insurance companies.
- (f) Corrosion of the substrate caused by intumescent coatings can be a problem. To avoid this microspheres have been used [6] to encapsulate corrosive ingredients thus rendering the coating non-corrosive.

1.2 Intumescent Mastics

The term 'intumescent' was first used by Olsen and Beche in 1948 [7], though

the first coating with such properties had been formulated ten years earlier. Intumescent materials have more recently been developed into four different markets, (i) as paints for short term protectors, often internally, (ii) as masks, often fibre reinforced for protection against fierce and longer lasting fires, (iii) as additives for plastics to render them fire resistant, (iv) as additives to ordinary paints to produce an intumescent paint (though this is not often successful).

The active ingredients of an intumescent coating are a polyhydric alcohol or resin containing sufficient hydroxyl groups, a source of phosphate or other dehydrating agent, a source of gas to foam the char, known as the spumific agent, and in most cases a catalyst, normally an amide, although this is less necessary when a condensed phosphate is included in the formulation.

In the basic formulation used in this work, the resinous material containing hydroxyl groups is the Aradite MY 753 epoxy resin, and Versamid (R) 125 hardener, the source of phosphate as fire retardant and acidic charring agent is supplied by melamine phosphate, which also acts as the spumific agent for foaming (from the melamine component) and the catalyst is provided by the hardener. Melamine orthophosphate is widely cited in patents for intumescent coatings.

There are many problems to overcome when developing an intumescent mastic, these include:

- (i) combining all ingredients to form a uniform mixture
- (ii) application of the viscous mastic to a substrate
- (iii) curing of the epoxy resin
- (iv) weathering resistance must be acceptable for outdoor application
- (v) minimum flammability of the coating itself
- (vi) aesthetic appearance, texture and colour associated with conventional paints would be highly desirable
- (vii) matching of the carbonific and spumific agents to ensure that each material

is used in an optimal fashion, leading to maximum yield of char.

The mechanism of intumescent reaction is:

- (a) release of free acid from its ammonium or amine salt
- (b) esterification of the polyol catalysed by an amide
- (c) melting simultaneously with esterification
- (d) decomposition of the spumific agent
- (e) charring commences simultaneously with gas release
- (f) finally the foam gels and solidifies.

The carbonific agent, the epoxy resin, would normally burn exothermically to produce oxides of carbon; and water vapour as its main products leaving as residue flammable tars. However, if the compound reacts with certain inorganic acids to produce an ester, the course of its thermal degradation is considerably changed. The degradation of cellulose has been extensively studied and parallels may be drawn with polyhydric acids [8]. Thermal analysis on the degradation of the phosphate ester of cellulose has shown the following changes [9].

- (a) the reaction becomes endothermic
- (b) flaming is reduced
- (c) flammable tars are not produced, instead a non-flammable char is produced
- (d) evolution of gaseous products is reduced in favour of char production.

Differential thermal analysis could be used to match the spumific and carbonific agent initially, though the combination would then have to be tested practically to ensure compatibility.

Because of the many problems associated with the use of intumescent coatings,

it is not possible to solve all the problems in any one formulation, but by assuming different formulation techniques, intumescent coatings fall into two main categories, paints for use internally, and resinous coatings, sprayed on as mastics, for external use. These are examined below:

- (a) Intumescent paints are normally applied as coatings of typical paint thickness, and can thus only protect the substrate for a short time. They usually exhibit a high degree of expansion, being used especially in fire doors or ventilation ducts where there is a specific requirement to close a gap and prevent fire spread. The active ingredients of intumescent paints do not behave well with respect to good paint characteristics, so much research has been carried out in developing multifunctional chemicals which can be used at low loadings, for example, a melamine-formaldehyde phosphate ester polyol [10]. Uniform cover must be achieved, such that the actual thickness is in no part significantly less than that stated nominal thickness. In addition, in the protection of personnel, it is important that emission of noxious fumes from the reaction of the intumescent paints are minimised. To achieve these desirable objectives for internal applications, the factors normally associated with good weatherability are no longer of importance.
- (b) Intumescent mastics are normally sprayed onto structural steelwork, and are suitable for the protection of flammable stores, petroleum tankers and chemical process equipment. The prime requirements are weatherability and resistance to damage by mechanical means. In such cases it has been found that formulations which enable these requirements to be met, normally produce noxious fumes on burning, and such coatings are not therefore suitable for the protection of personnel. Formulations based upon epoxy resin and phosphates of melamine are of this type, and many examples of formulations containing melamine phosphate and pyrophosphate are given in patent literature [11].

A coating with good weatherability is very important, recent patents suggest methods of overcoming the problem of water sensitivity by applying a solvent based overcoat for protection, though in some cases this may reduce intumescence.

1.3 Experimental Equipment

1.3.1 Fire Test Device

The Fire Test Device shown in Plate 1.1 and schematically outlined in Figure 1.2 consists essentially of a tunnel burner of face measuring 152 mm x 102 mm burning a mixture of air and natural gas. The sample to be tested, a 6 mm thick coating on a mild steel plate 95 mm square, is positioned facing the burner at a distance which may be varied to achieve a range of surface temperatures. The whole device is mounted on a Sindanyo¹ clad work bench. The test sample is mounted in a well, in a frame of Sindanyo, so that it is positioned in the same horizontal plane as the burner. This frame is constructed of four 6 mm thick layers of Sindanyo bolted together; the cut-out for the well in the outer layer is smaller by 6 mm along the sides and base than that in the inner layers. Into the groove thus formed along the top of the frame fits a block of Sindanyo of height 150 mm consisting of two 6 mm sections bolted together, which encloses and isolates the back of the sample from the burner. A sheet of 1.5mm mild steel is loosely bolted onto the front of the frame around the sample well at two points to give extra protection to the Sindanyo frame by reducing thermal stresses. The frame may be moved manually on horizontal steel bearers, lubricated by means of a spray containing aluminium and graphite in a non-drying medium. Rods of Tufnol² are attached at the back of the frame to enable it to be moved. The burner to sample distance, hereinafter known as its range, may be varied from 60 mm to 600 mm. Figure 1.6 shows how the temperature recorded by the two front face thermocouples compared with the real front face temperature over a range of distances from the burner.

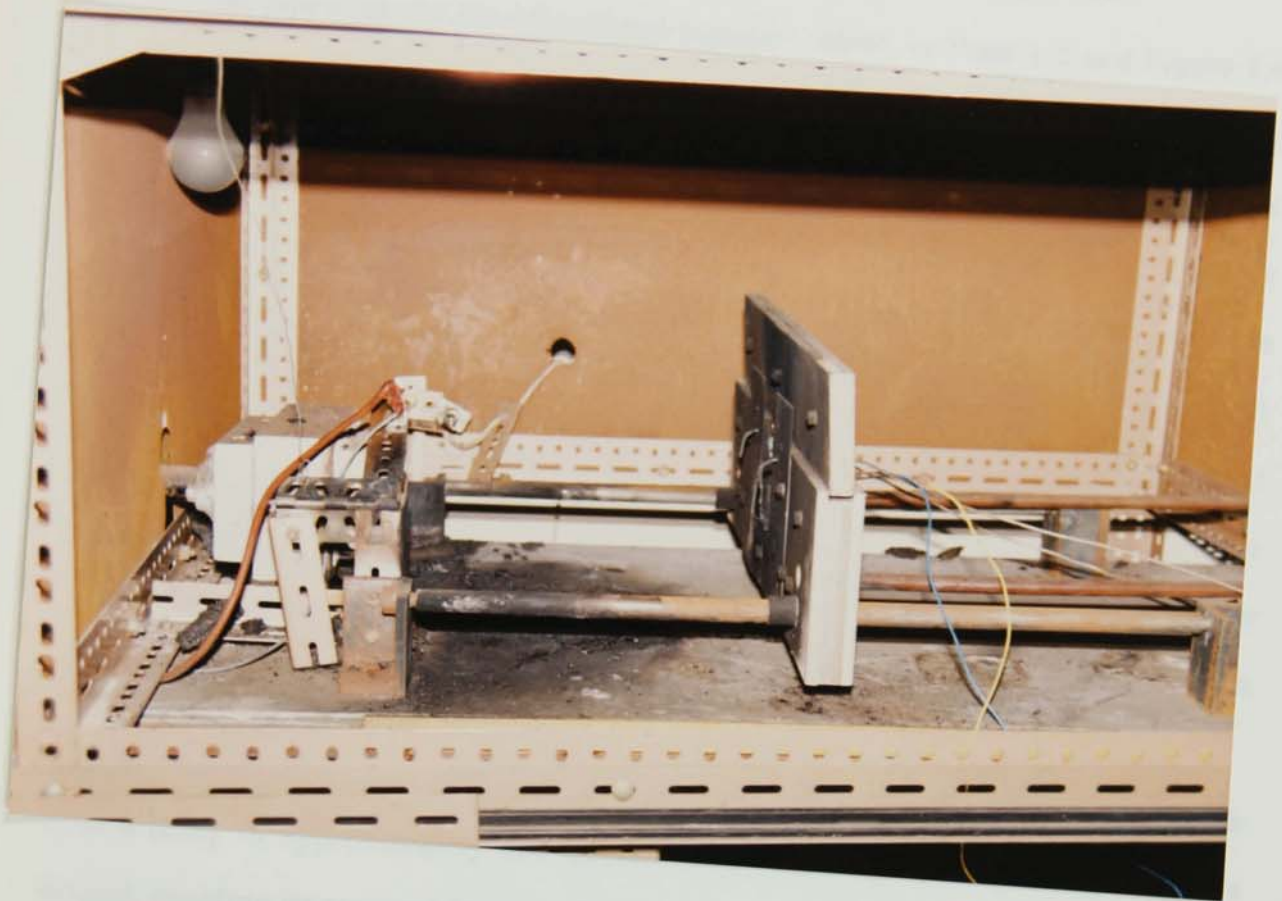
¹ Sindanyo is a registered trademark of TAC Corporation Materials Ltd

² Tufnol is a registered trademark

Schematic diagram of the fire testing device
(All measurements in mm)



PLATE 1.1
PHOTOGRAPH SHOWING THE FIRE TEST DEVICE



The working area is surrounded by an extraction hood, from which a duct leads via a bifurcated fan to the atmosphere. Sliding doors, of heat resistant glass, are provided in front of the working area; the other three sides and the ceiling of the hood are of 1.15mm mild steel sheet covered with aluminium paint for protection.

The pipework for the air and gas supplies shown in Plate 1.2 and Figure 1.4 incorporates several measuring and safety devices. Flowrates may be measured by means of rotameters, Type 18 with a Duralumin float for gas, and Type 24 with a Koranite float for air. Manometers are provided to read air pressure (by mercury), gas pressure prior to pressure reduction and after passing a 'zero' governor, and mixture pressure (all by water). Manufacturers instructions recommend an air pressure of 53 mm Hg which is achieved by a two stage reduction from the available compressed air supply. Typical values for gas pressure before and after reduction are 80mm water gauge and -10mm water gauge (ie. being entrained by the air stream); 140 mm water gauge is typical for the mixture. The gas to air flow rate ratio may be varied at the point of admixture.

Ignition is controlled automatically, being brought about by an electric spark after a delay of approximately one minute from initiation. The sparking device is hinged, enabling its removal from the flame after ignition by means of a wire attached to it leading to the front of the working area. An ultra violet sensitive photocell monitors the burner continuously and causes an immediate cessation of gas flow by means of a solenoid valve in the gas supply pipeline, should the flame fail at any time. The gas supply is also automatically shut off if the air supply is cut off or the electronic system switched off.

Schematic diagram of the Sindanyo Sample Holder, viewed from the Burner
(All measurements in mm)

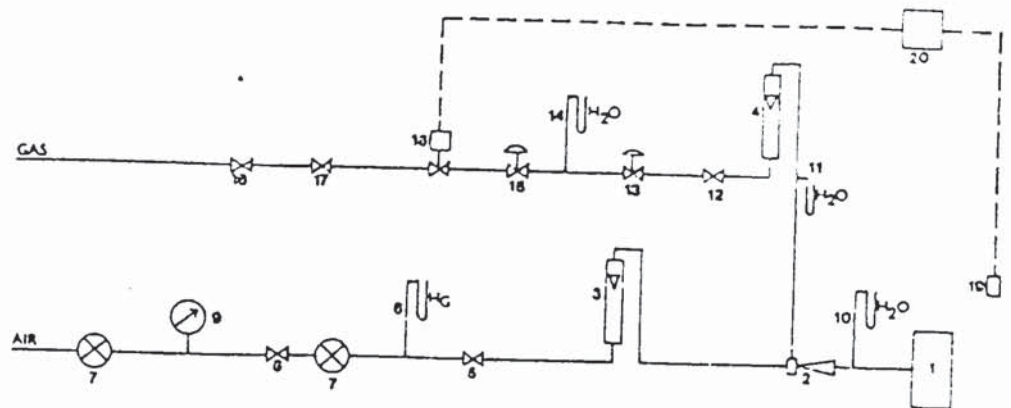
B Holes for thermocouples measuring face temperature

Technical drawing of a mechanical part, likely a bracket or support, showing dimensions and labels A, B, and C.

The drawing includes the following dimensions and labels:

- Overall Width:** 610
- Overall Height:** 43
- Top Flange Thickness:** 25.7
- Top Flange Width:** 163
- Label A:** Points to a rectangular cutout with a width of 105 and a height of 105.
- Label B:** Points to a rectangular cutout with a width of 105.
- Label C:** Points to a rectangular cutout.
- Other Dimensions:** 105 (width of the central section), 105 (height of the central section), and 105 (width of the bottom section).

FIGURE 1.4 : Schematic Diagram of the Air and Gas Supply Pipelines and Controls for the Fire Testing Device.



- 1 : Burner
- 2 : Air blast injector
- 3 : Air flow measurement; Rotameter, size 24
- 4 : Gas flow measurement; Rotameter, size 18
- 5 : Value with Butterfly Positioning
- 6 : Air pressure measurement, Mercury manometer
- 7 : Pressure Reduction Valves (Spirax)
- 8 : Shut-off valve
- 9 : Pressure gauge (0 - 100 p.s.i.)
- 10 : Mixture pressure measurement, Water manometer
- 11 : Gas pressure (reduced) measurement, Water manometer
- 12 : Shut - off valve
- 13 : Zero governor
- 14 : Gas pressure measurement, Water manometer
- 15 : Pressure control governor
- 16 : Solenoid operated shut-off valve
- 17 : Non-return Valve (otan)
- 18 : Shut - off valve
- 19 : Photo-cell
- 20 : Electrical control

PLATE 1.2
PHOTOGRAPH SHOWING THE GAS AND AIR SUPPLIES OF THE
FIRE TEST DEVICE

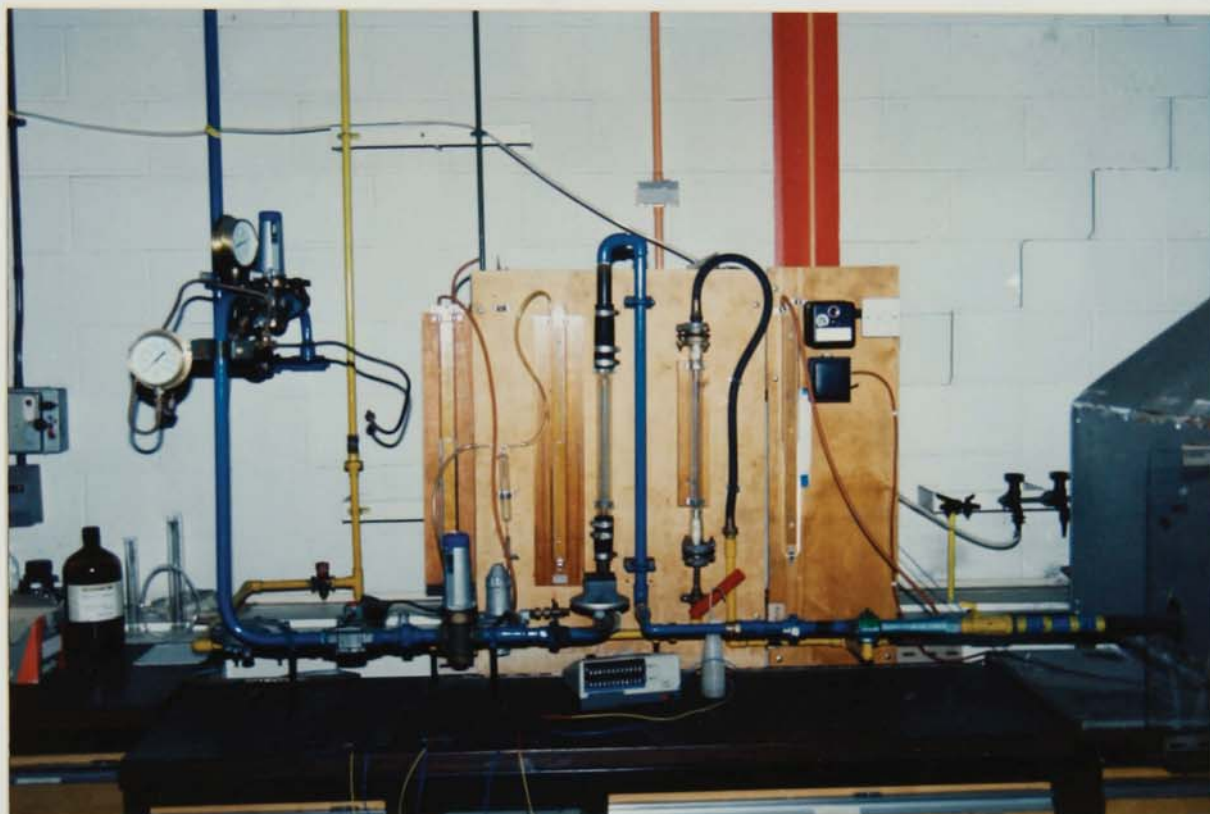
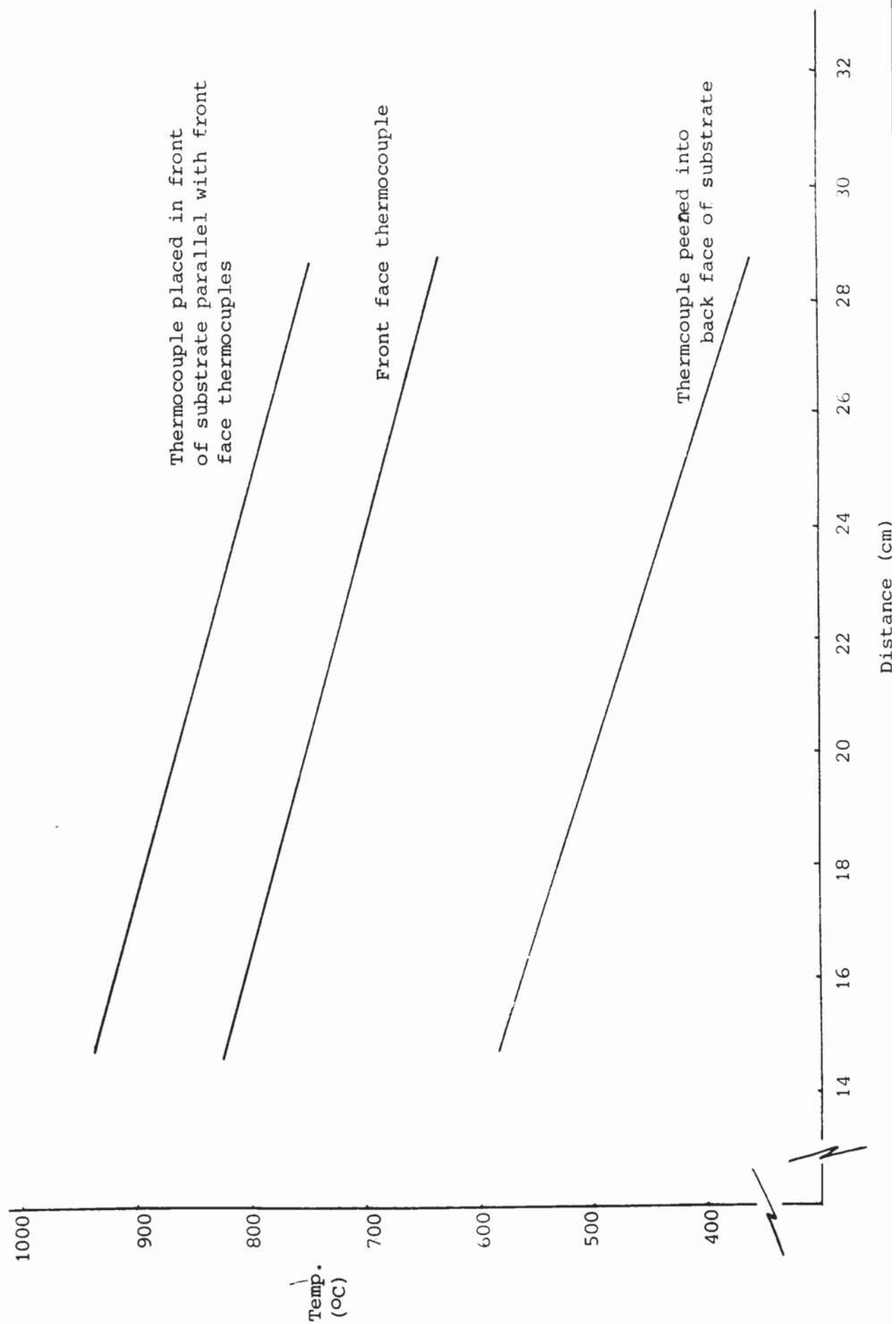


Figure 1.6 Relationship between temperature and distance between burner and sample



1.4 Temperature Measurement of Test Conditions

Two Chromel-Alumel thermocouples, mineral insulated to 3mm diameter and sheathed in Inconel³, pass through the Sindanyo frame at a height of 160mm above the Sindanyo working surface on either side of the sample. The projecting sections of the thermocouples are turned down to a depth of 15mm to minimise conduction losses. The thermocouple tips became blackened during the initial test, and remained thus.

It is very difficult to measure accurately the temperature of a hot gas by means of a thermocouple, the main causes of inaccuracy being:

- (a) radiation from the thermocouple to cooler surroundings
- (b) conduction down the thermocouple wires
- (c) the gas velocity
- (d) inaccuracies in calibration

The thermocouples incorporated in the Fire Testing Device were mainly to ensure the reproducibility of conditions, ie. that for a given sample range and burner conditions the temperature readings are similar on any occasion of use. Variation in the readings from the two thermocouples indicates an air flow across the face of the sample. The thermocouples are especially necessary when the sample range is varied during a test. Figure 1.6 relates the front face temperature with distance from the burner in the fire test rig. Normal operation temperature was 950°C.

1.5 Measurement of Substrate Temperature

1.5mm thick mild steel substrate had 2 thermocouples peened into the surface, one centrally situated, the other 2cm below, initially these were connected to the front face of the substrate and the wires brought through the substrate at the base of the sample, the insulation on the wires was destroyed during each test run, so other methods were tried, one such method was peening the thermocouple into the back of

³ Inconel (76/16/7 Nickel Chromium Iron) is a registered trademark of Henry Wiggin & Co Ltd

the substrate which assumes that, due to conduction through the substrate the temperature recorded at the front face is the same as that at the back. It was found that the temperatures recorded in both arrangements were the same, so the latter method was used for continuing tests.

The thermocouples were Ni-Cr/Ni-Al 0.376mm gauge wires of length at least 1.2 metres, sheathed in first ceramic bead insulation and then PVC sleeving.

During early tests, the thermocouples were connected to an 11 channel JP Electronics NiCr/Ni-Al thermocouple voltmeter, with a 0-5 volt output corresponding to temperatures in the range 0-2000°C with an error of ± 2 °C. The digital temperature read-out was noted at regular intervals, thus interrupting the continuity of visual observations of *intumesence*. This disadvantage was overcome by incorporating a BBC micro-computer in the system to record temperatures. However, the output from the thermocouple had to be adjusted from the 0-5 volt range down to the 0-1 volt range by use of 4 individual Comark temperature indicators (one for each thermocouple). The temperatures were then automatically logged by the computer at intervals of 10 seconds and simultaneously plotted on a graph of temperature against time, giving a hard copy at the end of each fire test. A photograph of the computer equipment may be seen in Plate 1.4. Examples of computer output are shown in Appendix 2, as is the computer program.

1.6 Video Monitoring

It was considered essential to have a visual record of events in order to derive maximum benefit from individual test runs. Previous work carried out [10] relied on taking 35mm picture stills taking pictures at regular intervals for further analysis after termination of the run. The more desirable method of obtaining a continuous record by movie camera was discounted on the grounds of cost. Experiments using a JVC Newvicon colour video camera and re-usable tapes proved highly effective; excellent

PLATE 1.4
PHOTOGRAPH OF THE COMPUTER EQUIPMENT USED
DURING FIRE TESTING



definition was obtained, leisurely and repeated examination of any selected section of the run was possible; and good copies of chosen frames could be obtained for permanent record. A running documentary could also be recorded simultaneously as the experiment progressed.

During recording the doors to the fire test rig were kept in place to maintain a reliable temperature profile, this did lead to a certain amount of image degradation. A major advantage of using this particular video system is the inbuilt realtime monitor (see Plate 1.3 for photograph of the video facility).

1.7 Methods of Mixing the Mastic

Two methods of mixing the system were tried in this research.

- (1) Standard method involved the use of a Kenwood Major Orbital mixer using an anchor stirrer until uniform on visual inspection. The main source of shear is within the components of the mixture itself; a smaller contribution arises between the mixture and walls. The degree of the mixture was found to depend not only on the vigour and time of mixing, but also upon the loading of melamine phosphate [10] and to a certain extent crystal size and shape; with less aeration for a 30% loading than for a 12½% loading, and for samples incorporating large crystals.
- (2) Manual mixing was another method tried, which allowed a different action of mixing which reduced the degree of aeration and allowed a more accurate visual and physical inspection of the mixed sample.

Other methods had been tried in previous work [10] using a roll mill and orbital mixer but were found to be successful for small crystals, only due to fracture with multiple millings.

PLATE 1.3
PHOTOGRAPH OF THE VIDEO FACILITY USED DURING
FIRE TESTING



Different percentages of melamine phosphates were included in a standard sample containing 39 g Aradite 5.6 g Versamide varying from 10% to 35% and the results are shown in Table 1.1.

The degree of fire protection depends solely on the char and so a method of grading the char was devised for future testing. Various weightings were placed on many characteristics, those thought to be of the most importance receiving a higher weighting/grade.

The scale is shown in Figure 1.5.

Table 1.1 Different percentages of melamine phosphate included in a 39g
Araldite and 15.6g Versamide sample

Percentage	Araldite (g)	Versamid (g)	Melamine Phosphate
10	39	15.6	5.5
12.5	39	15.6	6.7
15	39	15.6	8.18
20	39	15.6	10.9
25	39	15.6	13.6
30	39	15.6	16.3

FIGURE 1.5 Grading of char by weighing its characteristics

Characteristics	Grades	Relative weighing
Reflectivity of Surface	0-5	2
Uniformity of char structure	0-10	3
Extent of intumescence	0-10	1
Front face - time until degrades - strength of front face at 40 mins	0-10 5-10	2
Substrate temperature at 40 mins	0-10	2
Initial aesthetic appearance	0-5	2

Unmeasureable Characteristics

Fume production

Flaming during test

To estimate the quality of the char, multiply the grade scoring by the relative weighing, add all together to get total grade of char. A perfect char would score 100.

Extent of Intumescence is calculated by:

< 300%	6	
< 1500%	10	
> 1500%	6	Too much
> 2000%	2	intumescence

The uniformity of char structure can be calculated by:

% by 2mm diam	Score
10	10
25	8
50	5
75	3
100	0

Grading the front face temperature may be done by:

time at breakdown	Score
10 minutes	2
20 minutes	4
30 minutes	5

Gradeing the front face temperature may be done by:

Temperature measured by substrate thermo-couple after 40 minutes	Score
250-300	10
300-350	8
350-400	5
400-450	2

CHAPTER TWO
MELAMINE PHOSPHATE

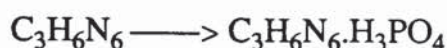
CHAPTER TWO

MELAMINE PHOSPHATE

2.1 Production of Melamine Phosphate

Melamine orthophosphate can be produced using various processes to obtain different crystal shapes and sizes; three main production routes are described.

- (a) Reaction at ambient temperature between a stirred aqueous suspension of melamine and phosphoric acid viz



A gelatinous suspension is encountered which on filtering produces small needles (10 μm).

- (b) Reaction at elevated temperatures between hydrochloric acid and melamine in equimolar preparations to form the hydrochloride, followed by the addition of monosodium orthophosphate to the suspension or solution, viz



The product suspension is considerably less gelatinous at both ambient and elevated temperatures; on filtering small reasonably well formed block plates are found.

- (c) Solution reaction at elevated temperatures with twice the quantity of hydrochloric acid specified above, followed by the addition of disodium-orthophosphate, viz



After complete addition of the disodium orthophosphate no precipitation is immediately evident. Very thin highly reflective plates of indeterminate size appear following a two minute induction period. A more detailed analysis of the production

routes to various crystal shapes and sizes is given below, and examined in more detail in work carried out by M Kay (10).

The following 'size range' descriptions have been selected for use in the rest of this work:

Small	< 20 μm
Medium	20 - 70 μm
Large	70 - 150 μm
Very large	> 150 μm

Furthermore, the aspect ratio, ie. the ratio of length to breadth of crystals obtained, is likely to be a necessary parameter in adequately describing crystals used in the intumescent mastics.

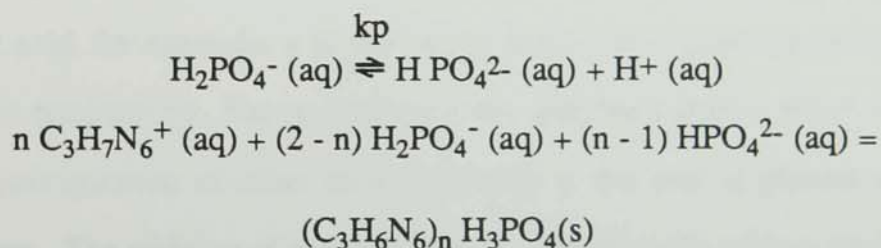
In the production of melamine orthophosphate certain parameters play a large part in determining the size and shape of the resulting crystals: these being temperature, concentration, relative quantities of reactants, degree of agitation of suspensions and cooling rate of solutions.

- (a) **Temperature:** the aspect ratio of crystals initially formed when immediate precipitation occurs on mixing of the reactants, increases with an increase in temperature. In reasonably dilute systems produced from equimolar quantities of melamine and phosphate, increase in temperature appears to reduce the thickness of the block plates produced, causing them to become highly reflective. Those precipitated at ambient temperature are thicker and non-reflective.
- (b) **Concentration:** generally an increase in concentration favours an increase in the aspect ratio of resulting crystals. Dilute systems tend to produce block plates (thin reflective at elevated temperature).

- (c) Relative quantities of reactants: a molar excess of phosphoric acid tends to increase the aspect ratio significantly.
- (d) Degree of agitation of suspension during reaction: as this increases so does the aspect ratio, though once the dispersion and reaction processes have reached completion, agitation has little or no effect on crystal shape.
- (e) Cooling rate from solutions of melamine phosphate at elevated temperatures. An increase in the cooling rate tends to promote plate formation, this is only really marked with a molar excess of phosphoric acid, a sufficiently fast cooling rate partially overcomes the tendency to form needles of a high aspect ratio, this may lead to the formation of thin reflective plate.

2.2 Stoichiometry of the Product

If melamine and phosphate are reacted in equimolar proportions, the product does not necessarily contain them in equimolar proportions, no matter what production route is followed. A typical molar ratio, n , is about 1.2 in the formula $(C_3H_6N_6)_n H_3PO_4$, but the ratio tends to be higher for the reflective plates normally produced from dilute systems. It has been found (10) that the molar ratio, n , of melamine to phosphate in the product depends upon the pH of the solution from which crystallization is taking place. The equilibria may be represented thus:



and the equilibrium constant for the dissociation of H_2PO_4^- k_p may be expressed by:

$$K_p = \frac{[\text{HPO}_4^{2-}] [\text{H}^+]}{[\text{H}_2\text{PO}_4^-]} = \frac{(n - 1) \cdot [\text{H}^+]}{(2 - n)}$$

therefore

$$n = \frac{2 K_p + [H^+]}{K_p + [H^+]}$$

Thus when a solution of melamine phosphate is cooled, as crystallization takes place, HPO_4^{2-} , is lost from the aqueous phase, but H^+ formed with it from dissociation of $H_2PO_4^-$ is not. The solution therefore decreases in pH as cooling progresses

and consequently the ratio of n decreases. As the solution becomes more acidic, the tendency to form needles rather than the reflective plates increases. The value of n obtained by chemical analysis is therefore a mean macroscopic value for the product, and will depend on the concentrations of the reactants, and the temperature difference between that at which crystals first appeared and the filtration temperature.

It was shown by Kler (13) that if crystals of melamine phosphate are left in their liquor after reaction, the pH of the liquor rises abruptly after around two weeks, from 4.8 to 5.2, at which it then stabilises, this indicates a reduction of n on storage in contact with water.

2.3 Affect of excess acid on Stoichiometry

If the reactant mixture contains excess acid, the consequent reduction in pH leads to a reduction in the value of n in the crystals formed. With a 25% excess of phosphoric acid, for example, n is reduced to 0.95-1.05 depending on concentration and filtration temperature. Excess hydrochloric acid has a similar effect, but there is a danger of precipitation of other melamine salts if the acid is present in sufficient concentration. The addition of monosodium phosphate to the system does not change the pH, and nor, consequently, the value of n .

2.4 Production of Specific Crystal Types

Needles of $(C_3H_6N_6)_{1.2} H_3PO_4$

Small needles are produced by adding a solution of phosphoric acid to a

vigorously stirred suspension of equimolar melamine, at ambient temperature. The material becomes highly gelatinous requiring vigorous stirring to prevent the viscosity rising, leading to needle-like crystals of aspect ratio around 5. Increasing the temperature of a concentrated system increases the aspect ratio of the needles and the viscosity of the system.

Small scale production commencing with 39.3g melamine in a 1.5 litre capacity reactor typically results in a yield of 78%. To produce large needles, average length 80 μ m of this stoichiometry, the solution containing equimolar quantities of melamine and phosphoric acid is cooled from solution at 90°C with minimal stirring. The product includes some block plates, but the majority of the crystals are needles of aspect ratio around five.

To produce needles of stoichiometry around $(C_3H_6N_6)_{1.0} H_3PO_4$ a reduction in pH is required, produced by the addition of 0.5% excess phosphoric acid. Large needles up to 30 μ m in length may be formed by cooling the solution from saturation at 100°C without stirring. Stirring leads to medium needles of around 50 μ m. If ambient temperatures are used the product will initially be in the form of small block plates or small needles of low aspect ratio, but will change to medium needles after a few hours.

Small Block Plates of $(C_3H_6N_6)_{1.2}H_3PO_4$

Small block plates are produced when melamine and phosphoric acid in equimolar quantities are mixed at ambient temperature with little or no stirring, they are considerably less gelatinous than small needles. However, a large scale operation is not feasible since thorough agitation would be required to effectively mix large quantities of reactants.

Other methods of producing small block plates are:

- (a) Leaving small needles in contact with their production liquor for several days; a process of mass transfer yields small block plates.

- (b) At ambient temperatures $\text{C}_3\text{H}_6\text{N}_6 + \text{HCl} + \text{NaH}_2\text{PO}_4 \longrightarrow \text{product}$
- (c) At ambient temperatures $\text{C}_3\text{H}_6\text{N}_6 + 2\text{HCl} + \text{Na}_2\text{HPO}_4 \longrightarrow \text{product}$
 though this method may lead to contamination of the product by melamine hydrochloride, also due to the gelatinous hydrochloride, encapsulation of unreacted melamine is a danger and warming would be necessary.
- (d) Replacing HCl with acetic acid, where the greater solubility of the melamine acetate intermediate and the plate like crystal shape of the acetate in suspension leads to a lower viscosity for this system compared to that for the hydrochloride. The major disadvantage of this system is the foam produced during agitation.

In a small scale batch production run at ambient temperature 59g of melamine and an equimolar quantity of hydrochloric acid were mixed in a volume made up to 0.75 litres. A solution containing 73.5 g of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ was slowly added and the volume made up to 1.5 litres, leading to a yield of 85%.

2.5 Laboratory Scale Production of Melamine Phosphate Reactor

A 3 litre cylindrical glass beaker was used for the small/laboratory scale production of all melamine phosphate crystal types thus enabling visual inspection during reaction, and helping to pinpoint possible problems that might arise on scale-up; for example, sedimentation. A paddle stirrer was used with an adjustable speed motor, the latter supported by a secure stand, not allowing excessive movement. The reactor temperature was controlled by a thermostat having a remote temperature sensor located within the reactor, attached to a flat plate heater on which the beaker rested. Complete reaction was determined by monitoring the pH of the system.

Filtration

The suspension was filtered using a Buchner vacuum filtration system with a 2 litre flask allowing a single filtration stage. The optimum thickness of filter cake formed was found to be 15mm, 2 Buchner funnels of 12cm diameter were required to handle one reactor batch. The cake produced was washed while still under vacuum suction, dried in situ, placed on a drying tray and crumbled to facilitate quick drying.

Drying

The wet cake was then dried at 110°C in a tray dryer until consecutive weighings showed no change in mass. The product was transferred to sealed containers for storage until required.

2.6 Heat Treatment

Yeadon et al (14) recommended heat treatment of melamine phosphate to reduce its solubility and hygroscopicity, various forms have been subjected to different temperatures and times of treatment showing that better intumescence was achieved following treatment at 210°C for 48 hours (10, 14). Higher temperatures and longer times resulted in an increased water uptake. Results obtained following differential thermal analysis of heat treated melamine phosphate (10) indicated that during heat treatment a change does occur to the melamine phosphate, hence the effect shown in fire tests when heat treated samples of melamine phosphate were used.

2.7 Analysis

There are three ways of analysing the melamine phosphate product:

- (a) chemical analysis, for melamine cation $C_3H_7N_6^+$ and phosphate anion $H_2PO_4^-$
- (b) microscopic analysis of the size and shape of individual crystals
- (c) fire tests, by incorporating the melamine phosphate crystals in a fire test sample and examining protectiveness of the resulting char.

(a) Chemical Analysis

2.7.1 Melamine cation $C_3H_7N_6^+$

A simple far ultraviolet spectroscopic technique is available for the melamine cation, which has two peaks at 210nm and 236nm respectively. The ratio of peak heights is approximately 3.2 at a pH of around 2, at which all samples should be analysed. A higher peak ratio indicates insufficient acidity as melamine itself has a larger extinction coefficient at 210nm, but does not absorb at 236 nm. A lower peak ratio is usually obtained when the absorbance of a particular sample at 210 nm exceeds 1.40 as above this value a linear relationship between absorbance and concentration is no longer maintained. Recalibration was not found to be necessary after the initial calibration had been carried out.

The solution of melamine phosphate (with a phosphorus concentration in the range of 0.02 mg - 0.2 mg/25 cm³) is diluted using 31.5-34% Analar hydrochloric acid to a pH of 2, normally around 0.5% V/V as a proportion of the total solution volume. (To use a less concentrated acid, dilution effects must be taken into account). Using a Pye-Unicam Sp 1800 spectrophotometer, an absorbance peak at 236 nm was produced and compared with a calibration curve for melamine, shown in Figure 2.1, and hence the melamine concentration in the sample found. The calibration graph had been produced using the same method.

2.7.2 Phosphate Anion $H_2PO_4^-$

This was measured colorimetrically using the method of Barnard and Chayer (64), once more samples require dilution to the range 0.02 to 0.2 mg of phosphorus/25 cm³. To an aliquot of the test sample in a 25 cm³ volumetric flask were added successively 1cm³ hydrochloric acid (31.5-34%), 2 cm³ of Amidol solution (1% diaminophenol hydrochloride and 20% sodium metabisulphate, filtered and kept refrigerated and away from light, must be used within 36 hours) and 1 cm³ of

ammonium molybdate, 8.3% solution. The volume was then made up to 25 cm³. The absorbance was read after twelve minutes at 700 nm, the upper wavelength limit of the Pye-Unicam SP 1800 spectrophotometer used. The blue coloration produced is due to a precipitate of molybdenum 'blue oxide' and the intensity of colouration is both time and concentration dependent. A standard calibration curve was produced using varying concentrations of monosodium orthophosphate dihydrate and recalibration was required on each occasion of use. The method is suitable for orthophosphate having an error of around $\pm 5\%$ greater than that in the determination of melamine cation.

Using this method the melamine and phosphate concentrations were measured independently, and then used to find the ratio n in $(C_3H_6N_6)_n H_3PO_4$. If each in turn was compared with the original melamine phosphate weighed for use in the analysis an error of $\pm 2-3\%$ occurred, probably caused by the melamine phosphate not going into solution completely. Tables 2.1 and 2.2 show examples of melamine phosphate analyses.

2.7.3 Photographic analysis

Using a sample, crystals could be examined for size and shape and photographs taken for later comparison, using a Zetopan optical microscope enabling both large and small crystals to be sized from photographs and scales.

2.8 Scaling-up the Production of Melamine Phosphate

If intumescent coatings containing melamine phosphate are going to be commercially viable the production of melamine phosphate must be expanded whilst still maintaining the same production conditions that are important on the small scale. Melamine phosphate has been produced in batches large enough to provide 4, 10 cm square, 5 mm thick fire test samples, ie. 100 g, but for commercial production substantially larger quantities would be necessary. With this in mind, the effect of scale-up was investigated, using a factor of 20, expanding the system from 1.5 litres to 30 litres.

Figure 2.1 Calibration curve for melamine analysis 236mm scale 0 -> 1

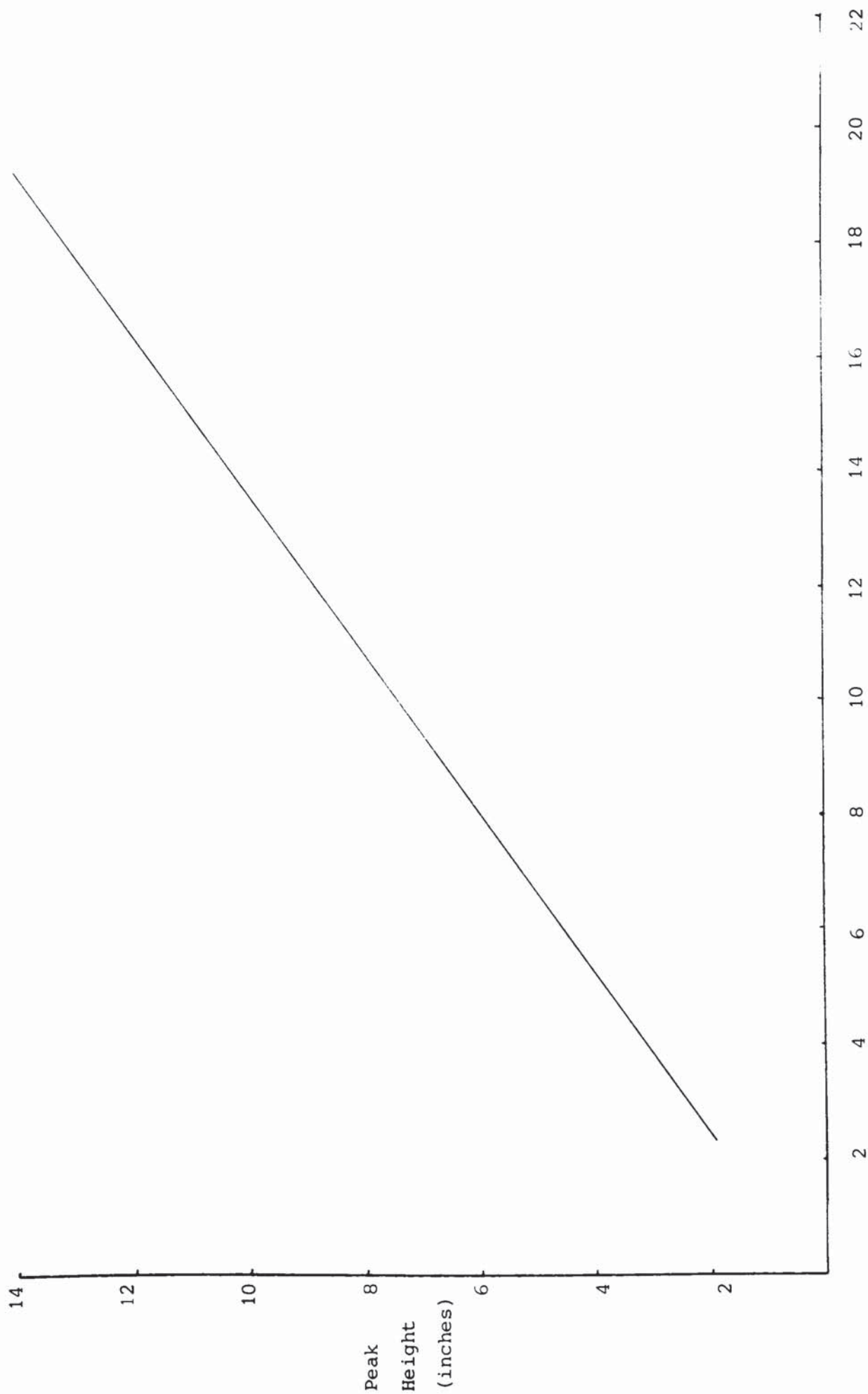


TABLE 2.1
RATIOS OF MELAMINE TO PHOSPHATE IN SEVERAL BATCHES OF
CRYSTAL TYPE PRODUCED FROM EQUIMOLAR PROPORTIONS OF
MELAMINE AND PHOSPHATE

Crystal type	Ratio of Melamine to Phosphate in product n	
	From current work	Work carried out by M Kay
Thin reflective plates	1.32, 1.33	1.30, 1.35, 1.31, 1.26, 1.29, 1.33, 1.30
Small block plates	1.21, 1.22, 1.19	1.20, 1.22, 1.21
Large needles	1.21, 1.23, 1.21	1.22, 1.22
Small needles	1.23, 1.23, 1.21, 1.24	1.25, 1.26

TABLE 2.2
RATIOS OF MELAMINE TO PHOSPHATE IN SEVERAL BATCHES OF
CRYSTAL TYPE PRODUCED FROM A 25% EXCESS OF PHOSPHATE

Crystal type	Ratio of melamine to phosphate in product n
Small block plates	1.10, 1.1
Large needles	1.11, 1.06, 1.14, 1.10, 1.01
Small needles	1.14, 1.11, 1.11, 1.10, 1.12, 1.02

Since different production methods were required to obtain the various crystal forms of melamine phosphate, three types were selected for scale-up work such that a wide-range of anticipated difficulties would be encountered. These included:

- (a) $(\text{C}_3\text{H}_6\text{N}_6)_{1.0}\text{H}_3\text{PO}_4$ large needles. Here elevated temperatures and high acid concentrations lead to problems.
- (b) $(\text{C}_3\text{H}_6\text{N}_6)_{1.2}\text{H}_3\text{PO}_4$ small needles. This production method could encounter difficulties in filtering.
- (c) $(\text{C}_3\text{H}_6\text{N}_6)_{1.0}\text{H}_3\text{PO}_4$ small block crystals. The HCl reaction route is used here.

Careful monitoring of the viscosity, temperature and pH at each stage of production was compared with the equivalent small scale production monitoring. And the finished product was analysed for the ratio of melamine to phosphate, the crystal size and shape, and the fire protective properties, once incorporated into the mastic. One problem which was not examined is rapid cooling of the bulk suspension, this is because only thin reflective plates require this and it has been found that these crystals are not suitable for intumescent coatings.

Apart from the above scale-up experiments, there were many more individual experiments to clarify a certain area, to retest values measured and to see if each production route is repeatable.

2.9 Problems that could be encountered with scaling-up

- 1 A cheap method of heating must be devised that is clean, and does not interfere with the stirring mechanism.
- 2 The stirring mechanism must have a high torque, variable speed indirect motor with a suitable impeller. Variable speed to allow for a change in melamine phosphate produced.
- 3 The rate of acid addition in any one area must be low enough so as not to

produce high viscosity pockets, this is particularly important in block plate production where localised mass transfer is the only permitted form of phosphate transport.

- 4 Small crystals could cause problems during filtering due to the possibility of blinding the filter. Continuous production methods do not appear to be feasible with the chemical system involved.

Reaction Vessel used During Scale up

Initially a 75 litre glass QVF vessel was used, a coiled electric heater was situated at the base of the tank, as was a 1.3cm diameter offtake. It was found that the heating coil interfered with the mixing, and the offtake was too small to allow passage of melamine phosphate agglomerates. Using this information a new stainless steel 45 litre tank was designed, of diameter 37.5cm, with a 5cm diameter offtake at the centre of a centrally sloping base. A 4.5cm baffle was inserted, and an impeller was constructed of stainless steel, with this a high torque, low variable speed motor was used. Plate 2.1 shows the above and Figure 2.3 shows a line drawing of the large scale production rig.

Solid Separation

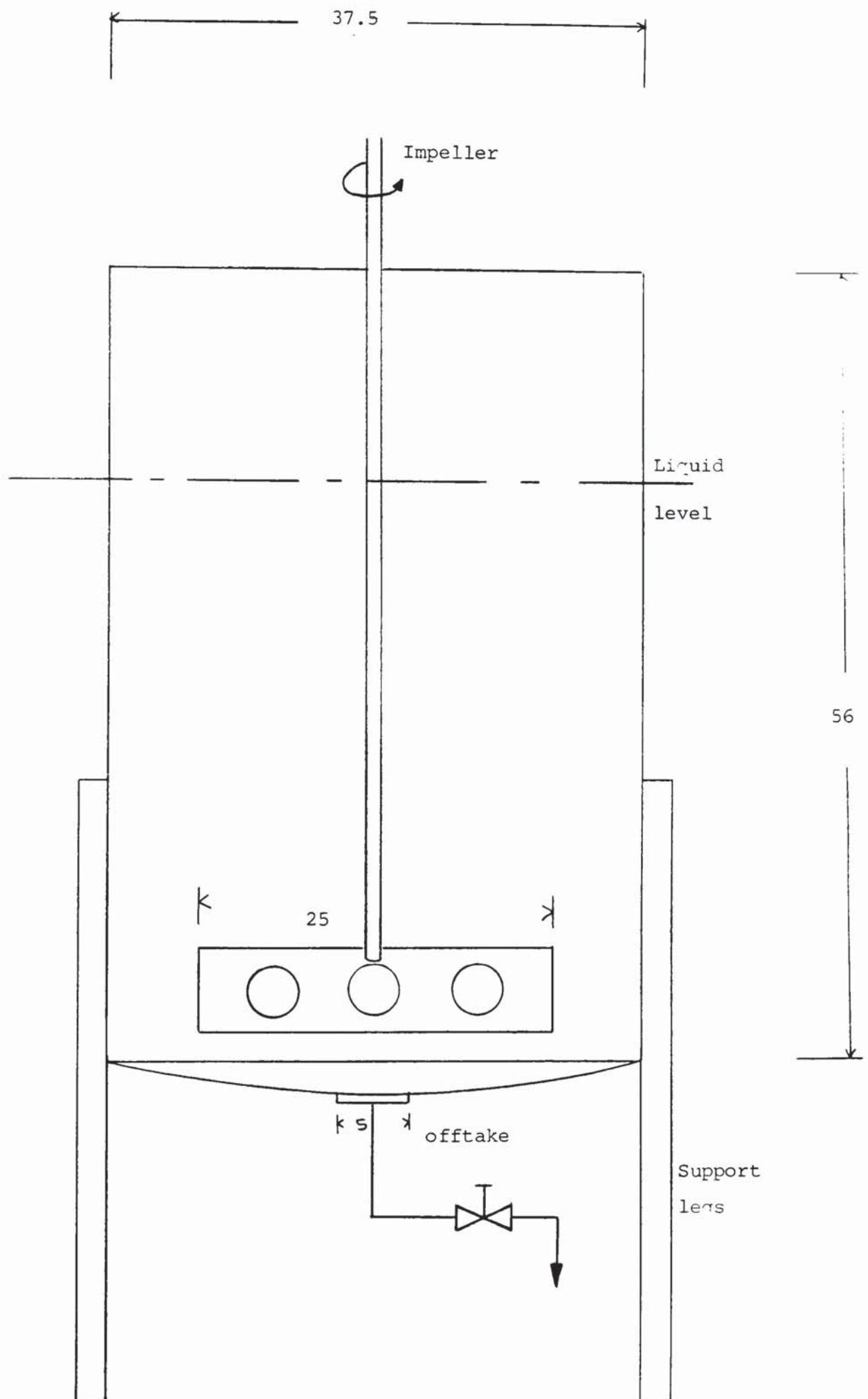
Due to the large volumes involved, decantation of the excess liquor after precipitation was found necessary. Vacuum filtration, using a 3 litre flask and Buchner funnel produced 12 filter cakes, 12cm diameter and 1.5cm deep. This was found to be very laborious, but a larger scale filtering system was not seen as a necessity at this stage.

2.10 Drying and Storage of the Product

Various methods of drying were tried, these are summarised below:

Figure 2.2

Schematic diagram of a large scale production ng
(All measurements in cm)



2.10.1 Batch tray and compartment driers

The driers used were similar to those used on the small scale runs, but larger trays (250mm x 450mm) were required and fabricated. These ovens operate using a circulating fan, but this was found to be impractical since once the solid had dried the small particles blew away. On a larger scale these would be less practical due to the high labour requirements associated with loading and unloading the ovens.

2.10.2 Vacuum driers

A vacuum tight chamber constructed of stainless steel was used, where the supporting shelves were heated to 80°C a vacuum applied and the water driven off was collected in a condenser.

2.10.3 Spray Drier

By decanting off only part of the excess water and creating a slurry, this feed can be sprayed in the form of small droplets into a heated drying chamber which was a vertical cylindrical vessel into which is fed large volumes of hot gas which dries the solid. The four main stages in the drying process are:

- 1 Atomisation of the feed suspension/solution
- 2 Spray-air contact
- 3 Drying of spray
- 4 Separation of dried product from gas (using cyclone)

The spray drier used was a Mobile Minor Niro atomizer (see Plate 2.2) spray drier unit, where the air brought in from the atmosphere flows co-currently with the spray and exhausted back into the atmosphere. A varied wheel rotary atomizer driven by compressed air is situated in the centre of the roof of the drying chamber. The slurry is fed by gravity (relying on a pump system on a high recycle flowrate to give good mixing) and dried product is separated from the exhaust stream by use of a cyclone. The air drawn into the system by use of a fan is then heated to 120°C using a variable electric heater. The variables in the drying operation were:

PLATE 2.1
LARGE SCALE PRODUCTION ng



- 1 Feedrate
- 2 Solids concentration in feed
- 3 Atomizer speed
- 4 Air inlet temperature

2.10.4 Fluid Bed Driers

To prevent caking of the solid, dry fluidised bed was used to which part of the filter cake could be continually added with continual take off. A fluidized bed was constructed from 3" QVF glass sections with a plastic mesh for the support plate and glass ballitini to aid distribution. To enable removal of solids from the bed an offtake valve was placed near the top of the bed. Wet solid was fed halfway up the freeboard zone and a cyclone separator collected any fines carried above the freeboard zone. An adjustable hot air blower was mounted below the distributor plate and was used for fluidising.

A sample which had been dried using a hot air oven (small scale) was used to make up the initial bed. The bed volume was gradually replaced by continual addition of wet 'large scale' melamine phosphate and removal of part of the bed, until 75% of the original material had been withdrawn and replaced by the new material.

See Plate 2.3 and 2.4 for diagram and of equipment used.

Storage

The increase in scale of operation offered no real problem as far as storage of the dry melamine phosphate, large plastic containers were used with tight fitting lids.

Experimental Results

(a) Batch drier

Using the 3 large trays available and a single oven (see Plate 2.4) it was found that normal drying temperature (120°C) took in excess of 48 hours to dry, due to the

PLATE 2.2

MOBILE MONOR NIRO ATOMIZER SPRAY DRIER UNIT



Plate 2.3 Diagram of experimental fluidised bed

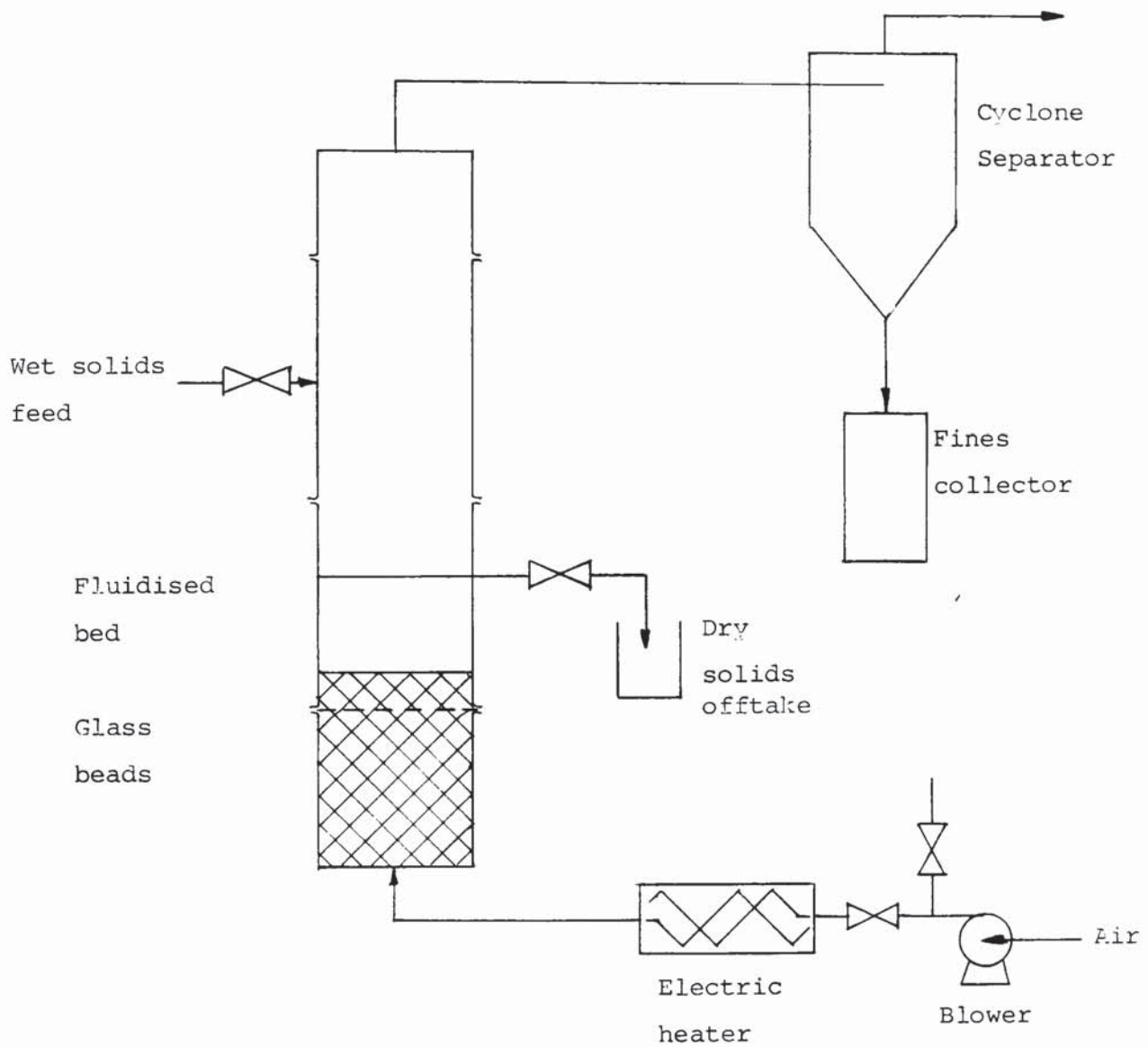


PLATE 2.4
PHOTOGRAPH OF THE BATCH DRIER USED



saturation of the hot air in the oven leading to condensation (and eventually flooding of the oven). This led to caking of the solids which on grinding down using a ball mill caused fracture of the large crystals.

Higher temperatures were used but this produced a discoloured hard cake which once more had to be ground down.

It was found (10) that some crystal types of melamine phosphate when in contact with their mother liquor for long periods, in excess of 24 hours their crystal size and form could change, so any drying method chosen had to be as short as possible.

b Vacuum driers

Once more the problem with drying the filter cake in the vacuum oven was found to be flooding of the system due to the high water loading and large quantity of solid.

c Spray drier

It was found that by adjusting the valve pressure 0.2-4 KP/cm² temperature (150-350°C) and feed rate that it was not possible to dry the solid properly, to use a higher temperature may cause degradation of the melamine phosphate. At high concentrations of melamine phosphate blocking of the passage lines was frequent due to agglomerates forming, this could cause problems on a larger scale and may cause particular problems in the atomiser of the spray drier.

d Fluidised bed

It was found that during the 'fluidised stage' (50 dm³/min) that 5/8 of the bed was stationary and tended to form agglomerates while the remaining 3/8 were highly fluidised fines. The static portion of bed increased as further melamine phosphate was added. It was found that there was no ideal gas velocity to prevent entrainment of fines and cause fluidisation. Table 2.3 lists the problems found and overcome during the scale-up reaction programme.

TABLE 2.3
PROBLEMS INVOLVED WITH THE SCALE-UP OF THE REACTION
PROGRAMME

<u>Problem</u>	<u>Solution</u>
1 Increase in viscosity on addition of acid (and hence problems in stirring).	As the initial increase in viscosity was due to localised reaction, better mixing was promoted by inclusion of baffles, larger more effective impeller and multipoint addition of acid.
2 Increase in temperature (and hence uncontrollability of crystal shape/size formed).	This was very difficult to monitor on the larger scale reaction due to the localised reaction, but with no mixing, it was quite apparent within the reaction area, therefore better mixing was encouraged using the same methods as above.
3 Visibly poor mixing	Inclusion of baffles. Larger more effective impeller. Use of variable speed indirect motor.
4 Solid separation	It was found, to decant off the excess liquor when the system had been allowed to settle was more time effective, then vacuum filtering of the remaining slurry.
5 Drying - due to changing crystal shape over an extended period of contact with mother liquor a quick drying method is necessary.	Possible use of rotary driers, drying at 120°C.

Analysis of the melamine phosphate produced during scale-up

(a) Batch ovens

The melamine phosphate dried in a batch oven was subject to case hardening, and it was found that it was necessary to use a ball mill to break down the agglomerates, this in itself caused fracture of larger needles. The resultant product when examined under the microscope was found to consist of both block plates and needles, this was thought to be because of the slow drying period and hence the transfiguration of crystal type from either needles to block plates or block plates to needles (depending on initial crystal type).

It was found during the fire testing of these samples, that under the same conditions the performance of the mastic was not found to have changed significantly, though the sample had a higher tendency to thermal cracking.

(b) Vacuum drier

Once more it was found that the crystals produced were not of the expected type, and by taking photographs of a large scale batch of small needles immediately after production, ie. before drying, it can be seen that it is during the drying process that the change takes place.

It is also found that the vacuum dried small needles when fire tested produced a poorer coating than a small scale sample.

It was found in both of the above cases that the ratio of melamine to phosphate was within the expected limit, ie. 1.15-1.25 when a ratio of 1.2 was aimed for.

Criteria for choosing the drying method

- (a) Time - due to the crystal shape/size changing while in contact with the mother liquor for periods in excess of 24 hours, the method chosen should dry the solid quickly, but must not form a hard crust, sometimes encountered at high temperature drying.

- (b) Temperature - as melamine phosphate breaks down when exposed to temperatures in excess of 250°C this is one constraint that must be imposed on the method chosen.
- (c) With such small low density particles removal of the fines from an exhaust stream is expensive so a drying method using a moving stream has limitations.
- (d) The method chosen must for economic reasons be machine rather than labour intensive, and must be capable of drying tonnes of wet solid per day.
- (e) The drying method must not interfere with the crystal size and shape, for example, grinding may cause fracture of larger particles.

CHAPTER THREE
COMMERCIAL SCALE PRODUCTION OF
MELAMINE PHOSPHATE

CHAPTER THREE

COMMERCIAL SCALE PRODUCTION OF MELAMINE PHOSPHATE

In the 'scaled-up' laboratory production, each run produced an average of 1 kg of dried melamine phosphate, which when incorporated into the mastic was sufficient to cover 1m² with a thickness of 5-6 mm. In a commercial environment it would be necessary to produce Melamine Phosphate in larger quantities, and hence a coverage area of 30 m² was chosen, requiring 30 kg batches of melamine phosphate. In laboratory scale manufacturing batchwise production was the only form considered as it was the simplest, but on larger scale-up where economics play a major part, both batch and continuous production must be examined for their relative merits.

3.1 Reactor Choice

When choosing the best type of reactor both the scale of operation and route of the reaction must be considered to allow comparison between the various types of reactor, both batch and continuous.

Chemicals normally produced in small quantities, for example pharmaceuticals and dyestuffs, are made batchwise. This normally allows a variation in product manufactured, giving greater flexibility where a large number of slightly different products are made on a relatively small scale. A further advantage of batchwise operation is that the capital cost is often less than for a corresponding continuous process when the desired rate of production is low. The reasons why continuous processes are often adopted in most large-scale chemical industries are mainly:

- a) Diminished labour costs, owing to the elimination of operations, such as the repeated filling, and emptying of batch vessels.
- b) The implementation of automatic control. This also reduces labour costs, although it usually requires considerable capital outlay.
- c) Greater constancy in reaction conditions and hence greater constancy in the

quality of product.

Before a choice can be made, it must be ascertained whether a continuous process, and hence a flowing system, may give rise to important differences in the kind of crystals produced. It must also be noted that a continuous process means that not all particles passing through the flow system will have equal residence times, nor undergo the same history of concentration or temperature changes, these factors may affect the mean reaction rate. Different types of reactors are given in Table 3.1.

3.1.1 Batchwise Reactors

This type of reactor would consist of a baffled and adequately agitated tank with the volume of reactants being 900 litres, inclusion of 40% dead space would bring the tank volume to 1.5 m^3 . Using a standard tank configuration, the diameter and height of liquid in the tank would be 1.046 m, and the height of tank 1.744 m. A dished base with central offtake ensures easy removal of tank contents, the offtake being flush with the inner surface of the tank. The impeller, an anchor stirrer would be a flat blade with curved bottom edge to follow the line of the tank allowing a 20 mm clearance, the width of blade allowing 10 cm clearance on the 10 cm baffles. A high torque motor would be required to allow for high viscosity mixtures, with an agitator tip speed of 2.5 m/s [18].¹ Sketches of both the tank and stirrer can be found in Fig 3.1. To allow for the system to be heated from ambient temperature to 100°C , a steam heating jacket should be incorporated. With a heating period of 1 hour the overall heat transfer coefficient, U , can be calculated [18] to lie in the range of $275\text{--}2750 \text{ W/m}^2\text{K}$, these U values could be reduced further by increasing the steam temperature from 100°C .

3.1.2 Continuous Production

There are various kinds of continuous reactor, for example, tubular or plug

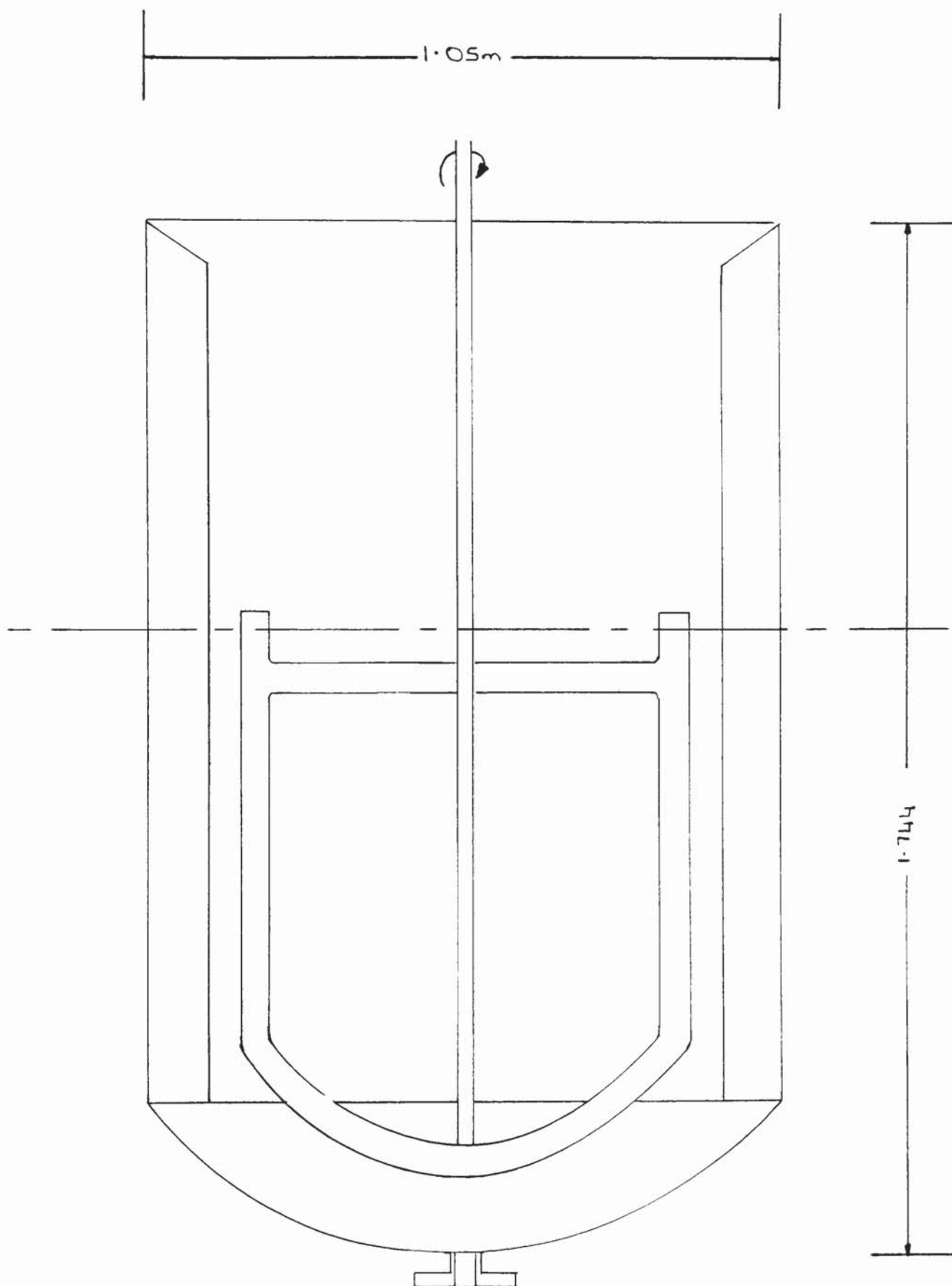
¹ The agitator tip speed is a measure of the degree of agitation in a liquid mixing system

TABLE 3.1
REACTOR TYPES

REACTOR TYPES	TIMES	TEMPERATURE VARIATION/CONTROL	MIXING	FOR HIGH VISCOUS SYSTEMS
C.S.T.R.	Unequal	Good	Good	Fair
Tubular	Equal	Good	Poor	Fair
Fluidised	Unequal	Good	Good	Good
Batch	Unequal	Good	Good	Fair

FIGURE 3.1

Large Scale Batchwise reactor



flow reactor, continuous stirred tank, fluidised bed reactor and many other diverse reactors.

3.1.2.1 Tubular Reactor:

A plug flow or tubular reactor is one in which all the reactants enter together, there is no back mixing across the axial plane. No attempt is made to induce mixing between elements of fluid at different points along the direction of flow, all reactants have the same residence time. If the reaction has a slow rate determining step the reactor is too long to be economically feasible. It has been found in the small scale production of melamine phosphate, that a reaction time of up to 25 minutes (pH monitored) was required and by assuming turbulent flow in the reactor, so as not to allow sedimentation, a reactor length of 7.5 km would be necessary. It is obvious that this is not a suitable reactor design.

3.1.2.2 Continuous Stirred Tank Reactor (CSTR):

This type of reactor consists of a well-stirred tank into which there is a continuous flow of reacting material, from which the (partially) reacted material passes continuously. The design of vessel must promote good mixing so preventing bulk streaming of the fluid between inlet and outlet resulting in bypassing, leaving the majority of reactor volume as deadspace.

It is assumed with CSTR that the contents are perfectly mixed. This is difficult with a viscous fluid phase. It is also an inaccurate approximation when solid particles settle out from the main liquid phase easily. A single CSTR or a chain of CSTR's has a great many advantages:

- a) Cheapness and ease of construction
- b) Ease of temperature control
- c) Openness of construction, so allowing easy access for cleaning the internal surfaces.

But because of the viscous properties of the system and the ease with which sedimentation occurs it was thought that a continuous stirred tank was not suitable.

3.1.2.3 Fluidized-bed Reactor:

This reactor can be used for reactions involving a solid and fluid (usually a gas), the solid particles are contained in a vertical cylindrical vessel and the fluid stream is passed upwards through the particles at a rate great enough for them to lift but not so great that they are prevented from falling back into the fluidized phase. This is only possible when the fluid and the particles are of considerably different densities, but this is not true for the melamine phosphate system. More detail is given in the fluidized-bed dryer section.

Reactor Conclusion

Assessing each of the reactor types it was concluded that only batch production was viable. Continuous production in a tubular reactor was not feasible due to its immense length, a continuous stirred tank is likely to give rise to an incomplete reaction, and to compensate for this a different production route would have to be chosen. To allow a flexible system, ie one which allow production of different kinds of melamine phosphate, and to limit the amount of a particular melamine phosphate produced, a batch reactor is the most appropriate choice, it enables this system to be carefully monitored and at the same time producing a known end result.

3.2 Liquid/Solid Separation

Once reaction is complete, the solid melamine phosphate must be separated from the liquid, dried and the particles separated into the size range 20-400 μm . It was found in small scale production that the particles tended to settle if not stirred, and often a preliminary decantation was necessary, here the suspension was filtered using batchwise vacuum filter, and then partially dried by drawing air through the filter cake. On a larger

scale this would not be cost, time or labour effective so a brief review of the current methods of industrial filtration was undertaken, the methods considered were:

- a) Clarification and thickening
- b) Flotation
- c) Sedimenting centrifuges
- d) Hydrocyclones
- e) Deep bed filters
- f) Cartridge filters
- g) Batch filters comprising of pressure vessel filters, filter presses, variable volume filters.

It must be noted that any filtering mechanism chosen must operate batchwise and have a quick turn-round time.

3.2.1 Clarification and thickening

In nearly all commercial cases gravity sedimentation operates continuously, the suspension is fed into one or more settling chambers, and while it is passing through the solids settle out, they are removed, together with a fraction of the liquid as thickened underflow, the rest of the liquids overflow. These are commonly called thickeners or clarifiers. Sedimentation devices can differ widely in size and configuration, normally however they comprise the following elements.

- 1 A tank to provide volumes, and area needed for clarification;
- 2 A system for introducing the feed and directing it into flow paths that will make effective use of the basin volume and area;
- 3 An overflow collecting system for gathering the clarified effluent in a way that will induce effective flow patterns;
- 4 A mechanism to convey settled solids to a discharge point.

This separation method has disadvantages for the melamine phosphate process because

(i) it operates more effectively continuously and (ii) it has a high residence time.

3.2.2 Flotation

This method may only be used where gas or air bubbles are attached to solid particles, resulting in a composite density lower than the liquid and hence rise to the surface where they accumulate as a 'float'. The success of this process depends upon two separate factors: one, the formation of an ample supply of suitably small bubbles and the other the attachment of the bubbles to the solid surface, which relies on the surface properties of the latter.

This particular method was thought unsuitable for the melamine phosphate system.

3.2.3 Sedimentary Centrifuges

Here the rate of settling of a suspension of solids is enhanced by the high gravitational field mechanically produced. All sedimenting centrifuges have essentially imperforate bowls (rotors) and the different types may be categorised according to the method of discharge of the solids. In all sedimenting centrifuges, solids will settle to the wall of the bowl and the clarified liquid (centrate) will discharge over a weir which is usually at the opposite end of the bowl from that at which the liquor is fed. In most major industrial machines, the centrate will discharge continuously once the bowl is filled and will continue to discharge until the feed is stopped. The solids may be discharged continuously, intermittently or in batches, depending upon the machine design.

It is an advantage in many situations to add a fast acting flocculent to aid separation and it has been found that in general, synthetic polymers with long chain molecules, and a high molecular weight produce high strength particles. This is not suitable where pure melamine phosphate is required as a component in intumescent coatings. There are 4 basic machine types:

- a) The high speed tubular bowl type with manual discharge of solids. Bowl diameters range from 5-15 cm and forces of up to 18,000 g are produced for industrial uses and 65,000 g for laboratory use. The bowl is fitted with a baffle

or accelerator to maintain the liquor at maximum speed. The feed slurry jets in at the base of the bowl, through the bowl neck, and, just inside the neck a distributor disperses the feed to prevent jetting too far up into the bowl. The centrate discharges from the top of the bowl by overflowing into a collecting cover.

- b) The skimmer pipe/knife discharge centrifuge uses a knife and pipe to discharge its solids. Bowl diameters range from 24-35 cm for a test machine and up to 150 cm for a large industrial centrifuge, with forces up to 1600 g, the feed enters at the bottom of the bowl, and the centrate discharges over a liping at the top.

The solids build up on the wall and once the clarity of the centrate is affected the machine is stopped and the solids discharged through ports in the bottom of the machine, first being knifed out.

- c) The disc centrifuge generates a settling force of up to 12000 g and is commonly used for clarification and thickening as the solids produced are in the form of a thick slurry, this may be discounted for this reason alone.

- d) The continuous scroll discharge centrifuge generally rotates about a horizontal axis producing a settling force up to 4000 g, the bowl diameter varying between 10 cm up to 200 cm, is normally cylindrical. Inside the bowl, a slowly rotating (2-100 rpm) helical screw transports the solids and discharges them from a conical section at one end of the bowl. This is an expensive machine to build and run and it was thought to be less suitable than types already described.

When choosing the type of centrifuge most suitable a number of factors must be considered:

- 1 size range of particles to be removed
- 2 speed the particles settle under gravity;
- 3 required performance, throughput, centrate clarity and cake dryness;
- 4 economic viability
- 5 characteristics of sedimented solids.

These are listed and compared in Table 3.2 [19].

3.2.4 Hydrocyclones are commonly known for their compactness, cheapness and versatility, they use centrifugal forces to aid sedimentation, the forces increasing as the diameter decreases, ie 800 g for a 30 cm diameter hydrocyclone, up to 50,000 g for a 1 cm unit. The performance of the hydrocyclones depends on the throughput and the density and shape of particles to be separated. On the whole hydrocyclones are used as classifiers only, not as collection devices.

3.2.5 Deep bed filters are used for the clarification of liquids, often to a very high degree of purity, normally the liquids to be purified are of very low concentration, usually less than 50 mg/dm³ and never more than 300 mg/dm³ and the filtrate concentrate may be as low as 0.1 mg/dm³. Their main use is in municipal engineering for domestic water supply and sewage treatment.

3.2.6 Cartridge filters are not normally selected for use if the filter cake is an essential part of the process, their design precludes anything but costly, inefficient means for collecting and disposing of the solids retained by the filter medium. It is found consequently that cartridge filtration is, in practice almost always limited to fluid polishing, producing filtrates of optical clarity or stentility.

3.2.7 Batch filters may be divided into three sections.

- I) Pressure vessel filters - of which vacuum batch filters may be regarded.
- II) Filter presses

Table 3.2
Classification of equipment according to
suitability

Type of Equipment	Scale m ³ /hr	Batch (B) or continuous
gravity separation	1 -> 100	C
flotation	1 -> 100	B
sedimentary centrifuges	10 -> 100	B
skimmer pipe	10 -> 100	B
disc	1 -> 100	B or C
scroll	1 -> 100	C
hydrocyclones	1 -> 10	C
deep bed filters	1 -> 10	C
cartridges	10 -> 100	B
batch pressure vessel with vertical elements	1 -> 100	B
pressure vessel with horizontal elements	10 -> 100	B
filter pressures	1 -> 100	B
variable volume filters	1 -> 100	B or C
continuous filters bottom-fed drum or belt drum	1 -> 100	C
top-fed drum	1 -> 100	C
disc	1 -> 100	C
horizontal belt pan or table	1 -> 100	B or C
pre wat drum	1 -> 100	C
bolt press	1 -> 100	C
delayed cake	10 -> 100	C
filtering contrifuge peeler	1 -> 100	B
pusher	1 -> 10	C
pendulum	10 -> 100	B
Oscillating and tumbling	1	C
warn screen	1	C

- III) Variable volume filters.
- I) Pressure vessel filters includes all filters in which the filter elements are located in a pressure vessel. As distinct from filter presses, filters of the pressure vessel type have the advantage that the material to be filtered is contained within a vessel that has a single seal, so that a cleaner, more reliable and more easily operated filter station results. This unit is ideal for a batchwise operation.
- II) Filter Presses comprise of a series of recessed plates referred to as filter elements, a framework provides support for filter elements, and a means with the framework for closing the elements together with sufficiently force on the sealing faces to counterbalance the applied force of filtration on the filtration area of the filter plates. The particular material is deposited on the filter medium and, if present in sufficient quantity, builds up to form a filter cake. When the filtration cycle is completed the closing force is released, the elements are separated and the filter cake is caused to discharge.
- III) Variable volume filters are ones in which two compartments are separated by an impermeable elastic membrane, and pressure applied by hydraulic fluid or compressed air in one compartment causing filtration in the other which is fitted with the filter medium. Once the pressure is released the cake discharges and a further cycle commences. Filtration pressure range form 10 to 100 bar.

3.2.8 Centrifugal Filters

See Table 3.3 for the operating ranges of the main types of centrifugal filters, it can be seen that only the Peeler and Pendulum operate over a suitable size range, the peeler being emptied at higher speed, and the pendulum being a rigid mounting in housing which is hung with penduli, both producing a good quality product of low residual moisture, and both operating batchwise. The horizontal peeler having a higher throughput than the vertical peeler [19].

Continuously operating centrifuges are best utilised in separating quickly-

Table 3.3
Operating range of main types of centrifugal filter

Type of centrifuge	continuous	automatically discharged at full speed	automatically discharged at reduced speed	g-factor range (F_c)	minimum solid concentration in feed. % by volume (C_v)	possibility of washing	minimum particle size, mm	minimum filtrability coefficient (k)(m/sec)	minimum retention time, seconds
Oscillating	X			30-120	40	no	0.3	5×10^{-4}	6
Tumbler	X			50-300	40	no	0.2	2×10^{-4}	6
Worm screen	X			500-3000	20	poor	0.06	1×10^{-5}	15
Pusher	X			300-2000	30	good	0.08	5×10^{-5}	60
Peeler		X	X	300-1600	5	very good	0.01	2×10^{-7}	as wanted
Pendulum			X	200-1200	5	very good	0.005	1×10^{-7}	as wanted

filtered products with a high solid concentration, while batch operated ones allow a greater variation in drum speeds, product washing and dry centrifuging. This facilitates qualitative optimisation of the processed products and adjustment to varying product parameters.

Conclusions

A batch or semi-batch separation process would be the most applicable method where a batch reaction system has been adopted, sedimenting centrifuges, batch and centrifugal filters are the most appropriate. By comparing each of the methods it was found that the centrifugal filters particularly the pusher and peeler types are capable of handling a high throughput of high solids content (30% by volume in the Peeler) [19]. With the residual moisture content of the cake being 18-22% [19]. Sedimenting centrifuges produce a 'cake' with a maximum solids content of 50-70% and batch filters of 35-70%.

3.3 Drying of the Melamine Phosphate

A wide variety of dryer designs have been evolved over the years to cope with various situations, those relevant to the drying of melamine phosphate are compared below.

Batch tray and compartment dryer

The most generally used intermittent drying ovens usually employ trays on which the wet material is supported, and which are loaded either onto trucks in tiers or are inserted directly into the dryer in which they are supported on tiers of angle-iron supports. Heated air is circulated by means of fans over the wet material, and the humid air is rejected to the atmosphere. Once drying is complete, the trays are emptied and recharged with the next batch. Another form of heating used is indirect by use of heated shelves, radiator coils, or refractory walls inside the insulated housing, here circulation of

a small quantity of gas is usually necessary to prevent gas saturation and condensation.

Batch tray dryers have a limited field of application due to the high labour requirements associated with the loading and unloading of trays. This may only be seen as economically viable where a long heating cycle is required, because of the size of solid objects, or permissible heating temperature requires a long hold-up for internal diffusion of heat and moisture: the production of several different versions of the same chemical requires strict batch identity and thorough cleaning of equipment between batches; the quantity of material to be processed does not justify investment in more expensive continuous equipment. Also because of the nature of solids-gas contacting, usually via parallel flow, as opposed to circulating flow, heat and mass transfer are comparatively inefficient.

3.3.2 Vacuum-shelf Dryers

Vacuum-shelf dryers are indirect-heated batch dryers consisting of a vacuum tight chamber usually constructed of cast iron or steel plate, with heated supporting shelves within the chamber, a vacuum source and usually a condenser. Hollow shelves of flat steel plate are permanently fastened inside the vacuum chamber and are connected in parallel to the inlet and outlet manifolds. The heating medium, passing from the inlet manifold through the hollow shelves to the exit manifold can be steam or hot water depending upon the temperature required, some dryers use electrically heated shelves.

1-24 shelves normally of metal to ensure good heat transfer make up a tray drier. A large pipe to remove vapour is connected in such a way, that with a break in vacuum the sudden air inflow does not disturb the material. The vapour is removed from the exiting stream and the non-condensable gas goes to the vacuum source.

Vacuum dryers are used extensively for drying pharmaceuticals, temperature sensitive or easily oxidisable materials and dusty materials may be dried with negligible dust production.

3.3.3 Agitated Batch Dryers

The agitated batch dryer is essentially a heated vessel, either a vertical (pan) or horizontal (cylinder) in which the material to be dried is agitated whilst in contact with the heated metal wall. The moisture is removed either at atmospheric pressure, or under vacuum. In the vertical type, agitation is provided by a paddle agitator, whilst in the horizontal type by either a scroll agitator, or quadrants and rollers. The quadrants and rollers provide simultaneous grinding and mixing.

For drying under atmospheric conditions, pressure steam is the usual heating procedure, and under vacuum conditions pressure steam, sub-atmospheric pressure steam, or hot water can be used. Any of the usual metals can be used as the material of construction, but in general cast iron or mild steel have been used for the vertical and mild steel or stainless steel for the horizontal type.

For operation at atmospheric pressure ancilliary equipment may simply consist of a vapour duct and chutes for charging and discharging material; for operation under vacuum the equipment will include condenser, cyclone separator or heated filter, vacuum pump, hot water circulation system or temperature controlled steam supply.

The agitated batch dryer can be used to dry most materials, either in paste or slurry form, at a relatively low operating cost since labour requirements are small. For a given batch size it provides the cheapest form of non-continuous drying.

Generally this type of dryer is best suited to the drying of materials which are friable (liable to crumble) and which do not pass through an extremely viscous stage during the drying process. The cleaning of each type of machine vertical and horizontal is relatively easy, but multi-product operation in single batches is not normally employed because of the hold up of material (2% of batch weight) on completion of drying.

3.3.4 Spray Drying

Spray drying involves the transformation of a feed material into dried particulate form by spraying the feed, in the form of small droplets into a hot drying chamber. The

drying chamber is a large cylindrical, and usually vertical, vessel into which is fed a large volume of hot gas (usually air) which rapidly vapourises the liquid (usually water) leaving particles of solid which must then be separated from the gas. The motion of the gas can be either co-current or counter-current. (The drying gas and evaporating liquid will hereafter be referred to as air and water as would be found when drying melamine phosphate.)

The characteristics of the dried product are variable and depend upon the operating conditions, and how each of the spray drying stages listed in chapter 2 are incorporated into the spray dryer design, together with the physical and chemical properties of the feed.

The materials which can be fed to a spray drier are generally those materials which can be handled as liquids in pipes. Thus solutions, emulsions, suspensions and slurries can all be spray dried. Gravity feed systems are often adequate, the head tank being stirred if necessary: otherwise the feed liquor may be pumped to the atomiser.

3.3.4.1 Atomisation

Atomisation involves the breakdown of the liquid bulk into many individual droplets forming a spray. On contact with the hot gas this gives rapid evaporation conditions due to the vast surface area of droplets in a spray (for example 1 cubic metre of liquid forms $\sim 2 \times 10^{12}$ uniform 100 μm droplets which offer a total surface area of 60,000 m^2). Thus the atomisation stage in spray drying must create a spray that gives optimum evaporation conditions. A wide variety of spray characteristics can be obtained for a given product through combinations of feedrate, atomizer speed and atomizer design.

Two types of atomizers available are rotary atomizers, and nozzles. Rotary atomizers come in two categories: atomizer discs and atomizer wheels, and one of the most important features is the ease of particle size control merely through wheel-speed control. Atomizer discs are used to meet coarse-spray requirements while atomizer

wheels are used for the fine to medium-coarse size range. Designs of discs include vaneless plates (ie discs) cups and inverted bowls (a degree of slippage of the liquid film occurs on vaneless discs giving a lower peripheral velocity), and designs of wheels have vanes or bushings (bushings used in specialised fields).

Rotary atomizers are reliable, easy to operate, can handle fluctuating feed rates (and abrasive feedstocks) and can handle high feed-rates without atomizer duplication. Atomizer wheels have negligible clogging tendencies due to large flow ports, and produce sprays of good homogeneity. Rotary atomisers are used to produce spray of mean size 30-120 μm .

Nozzle atomizers come in two forms: pressure nozzles and two fluid nozzles. With a pressure nozzle the feed material is fed to the nozzle under pressure, the pressure energy is converted to kinetic energy, and feed issues from the orifice as a high speed film that readily disintegrates into a spray. The feed is made to rotate within the nozzle using various inserts, or by tangential flow entry, to produce a cone-shaped spray emerging from the nozzle orifice.

With the two fluid nozzles, the feed material and the atomising air are passed separately into the nozzle head. High air velocities are generated within the nozzle to give effective feed contact which breaks up the feed into a spray of fine droplets. Sonic velocities are often generated. The air stream is rotated within the nozzle, and feed is either contacted within the nozzle, or as the liquid emerges from the orifice.

Sprays from pressure nozzles handling high feedrates are generally less homogenous and coarser than sprays from vane wheels, but at low feed-rates spray characteristics from nozzles and wheels are comparable. Duplication of pressure nozzles allows fine sprays to be obtained, but nozzles are generally used to form coarse particle powders (mean size 120-250 μm). Variation in pressure gives control over feed-rate and spray characteristics. Swirl inserts in a pressure nozzle have fairly large flow passages and enable such nozzles to handle high solids feed (such as that found in the production of melamine phosphate) without undue wear or clogging.

Two fluid nozzles have the advantage of handling high viscous feeds producing sprays of medium coarseness, but of poor homogeneity. For low viscosity feeds, fine particles can be produced, although the resulting dried powder may be of agglomerates. There is a high likelihood of occluded air content within the particles. Two fluid nozzles are expensive to operate and low production per dryer unit is obtained (and are thus used mainly in small-diameter pilot plant chambers).

3.3.4.2 Atomizer Selection

The selection of atomizer type depends upon the nature of the feed and desired characteristics of the dried product. In all atomizer types, increased amounts of energy available for liquid atomization results in sprays having smaller droplet sizes. If the atomisation energy is kept constant but the feed-rate is increased, sprays having larger droplet sizes will result. The degree of atomization also depends upon the fluid properties of the feed, where low values of viscosity and surface tension result in smaller droplet sizes for the same amount of available energy for atomization, when either a rotary or a nozzle atomizer is available; the rotary atomizer is normally selected due to its greater flexibility and ease of operation.

3.3.4.3 Spray-Air Contact (Mixing & Flow)

The manner in which the spray contacts the drying air is an important feature in spray drier design, as this has great bearing on dried product properties by influencing droplet behaviour during drying. Spray-air contact is determined by the position of the atomizer in relation to the drying air inlet.

In co-current flow, the spray can be directed into the hot air entering the drying chamber. This arrangement is widely used, especially if heat-sensitive products are involved. Spray evaporation is rapid, and the drying air cools as a result. This means that the product is not subject to heat degradation due to the basic physical principle of "evaporation causes cooling", so that product temperature is low during the time the bulk of evaporation takes place, and when the desired moisture content is being approached,

each particle of the product does not rise substantially in temperature because it is then in contact with much cooler air. Thus low temperature conditions prevail virtually throughout the entire chamber volume in spite of very hot air entering the chamber. However, the rotary atomiser allows the radial trajectory of droplets from the atomiser periphery to be controlled, so excessive product deposits on the drying chamber wall are prevented.

In counter-current flow, spray and air enter at opposite ends of the dryer. This arrangement subjects the driest powder to the hottest air stream. It readily meets granular powder requirements of non-heat sensitive products. Counter-current flow is used with nozzle atomisation, since an upward streamline flow of drying air reduces the downward velocity of the large droplets in the spray, giving sufficient residence time for completion of evaporation.

There are dryer designs that incorporate both co-current and counter-current layouts, i.e. mixed flow dryers. This type of dryer gives coarse free flowing powder produced in drying chambers of relatively small size, but the powder is subjected to higher particles temperature.

How best to contact the spray cloud with drying air is dependent upon the product involved. In the case of melamine phosphate which is relatively heat sensitive, a co-current spray drier would be chosen. Co-current flow gives a product temperature of 15-25 °C lower than the outlet temperature of the spray drier.

3.3.4.4 Drying of Spray

As soon as droplets of the spray come into contact with the drying air evaporation takes place from the droplet surface, which approximates to the wet-bulk temperature of the drying air. Evaporation takes place in two stages, at first there is sufficient moisture within the droplet to replenish that lost at the surface. Diffusion of moisture from within the droplet maintains saturated surface conditions and as long as this lasts evaporation takes place at a constant rate, this being the constant rate period of

drying. When the moisture content becomes too low to maintain saturated conditions at the particle surface, the critical point is reached and the particle presents a dry surface. Evaporation is now dependant upon the rate of moisture diffusion through the dry particle surface. This is the falling rate period of drying. From this it can be seen that a substantial part of particle drying takes place when the particle surfaces are saturated and cool.

Drying chamber design and air flowrate provide the droplets residence time in the chamber, so that the desired droplet moisture removal is achieved, and the product removed from the dryer before product temperatures can rise to the outlet drying air temperature of the chamber. Hence there is little likelihood of heat damage to the product.

During evaporation, the atomised spray distribution undergoes change. Different products exhibit different evaporation characteristics. In the case of a suspension, sometimes the product may fracture or disintegrate leading to irregularly shaped particles. The extent of any change in particles shape is closely related to the drying rate, thus close consideration must be given to the drying chamber design.

3.3.4.5 Separation of Dried Product from the Air

Two systems are used to recover the product, in one system primary separation takes place during drying where the coarser particles fall to the base of the chamber and the fines are entrained in the air and collected in dry collectors such as cyclones, bag filters or electrostatic precipitators, followed (if necessary) by wet scrubbers. In the other system, dried product removal takes place in the separation equipment, which places great importance on the separation efficiency of the equipment (but this system is often utilized as it does not need a product conveying system).

3.3.5 Fluidisation

The major parts of a fluidized-bed system can be listed as follows:

1. Reaction vessel
 - a) fluidized-bed portion
 - b) disengaging space or freeboard
 - c) gas distributor
2. Solids feeder or flow control
3. Solids discharge
4. Dust separator for exit gases

It is noteworthy that many of the same problems exist in fluidised bed dryers that exist in fluidised bed reactors.

3.3.5.1 Reaction Bed Vessel

a) Fluidised bed portion

The process of fluidizing converts a bed of solid particles into an expanded suspended mass that resembles a boiling liquid which seeks its own level, and assumes the shape of the containing vessel. Space must be provided for vertical expansion of the solids and for disengaging splashed and entrained material (freeboard). The usual shape is a vertical cylinder, but there is no limitation in shape (but the lack of moving parts tends towards a simple clean design). The total cross-sectional area is determined by the volumetric flow and the required fluidising velocity of the fluid at the operating conditions. The minimal velocity is best determined by test equipment where visual observations of the action of the bed can be made. The flow required to maintain a completely homogenous bed of solids, where-by coarse or heavy particles will not segregate from the fluidised portion is very different from the minimum fluidising velocity. The maximum flow is generally determined by the carry over or entrainment of solids, and this is related to the cross-sectional area and height of the disengaging space.

b) Freeboard

The free-board or disengaging height is the distance between the top of the

fluid-bed and the gas-exit nozzle. There are two ways in which solids enter the freeboard, either from splashing or from entrainment of the finer particles. Splashing occurs when a fluid bubble reaches the upper surface of a fluidized bed, breaks through the thin upper envelope composed of solid particles, entraining some of these particles. The crater shaped void formed is rapidly filled by flowing solids, when these solids melt at the centre of the void, solids are thrown upwards. These solids along with the entraining fine particles enter the freeboard where the larger and denser particles disengage from the upward-flowing gas and return to the top of the bed, and the finer and lighter particles are carried away.

c) Gas distribution

For efficient fluidization it is essential that the drying gas is distributed uniformly under and throughout the whole bed. Distribution will be uniform if the pressure drop across the distributor is sufficiently high, generally at least equal to the pressure drop through the bed. The design of distributor plates varies, some are perforated with holes about 1 mm diameter, other use slots, and yet others use bubble-plate type distributors. When perforated plates are used, it is preferable to dish them (centre down) in order to increase the flow of gases near the walls of the vessel since the normal tendency is for higher flows at the centre of the bed. This arrangement also facilitates emptying the vessel.

Porous porcelain tiles or glass beads also serve as excellent gas distributors when the required fluid velocity is low.

In order to reduce back flow of solids when a plant is shut down, the gas flow should be stopped by a valve after the blower and the pressure relieved from the bottom upward through the bed; if the blower is tripped electrically, dusty fluid flows down through the distributor and out through the blower.

3.3.5.2 Solids Feeding & Flow Control

The feed is introduced into the drying chamber at the top of the fluidised bed. An essential feature of any arrangement for feeding material is that the material is in a

dispersed form. This is because agglomerates are large particles which will sink to the bottom of the bed of smaller particles unless they break up immediately they arrive on the bed and begin to dry. If the agglomerates do not break up, then in time the whole of the fluidised bed may be replaced with a static bed of agglomerates.

Suitable feed mechanisms are screw-type feeders, star feeders and rotary valves, but only the first can deliver material into a region of high pressure. When the moist material is free flowing it can be fed from a steeply sided supply bunker down a wide pipe, terminating near the base of the bed. The bunker can then be fed by any form of conveyor suitable for the moist material. The supply leg from the bunker acts as a gas seal. It is also necessary to use a feed system which enables the rate of feed to be metered in order to match the feed-rate with the evaporation rate of the system.

3.3.5.3 Solids Discharge

The type of discharge mechanism utilised is dependent upon the necessity of sealing the atmosphere inside the fluidised bed dryer and the subsequent treatment of the solids. The simplest solids discharge is an overflow weir. This can be used only when the scope of fluidising gas does not present any hazards due to its nature or dust content, or when the leakage of gas into the fluidised bed chamber, from the atmosphere into which the bed is discharged, is permitted.

Where it is necessary to restrict flow of gas through the opening, a simple flapper valve is frequently used. Seal legs are frequently used in conjunction with solids flow-control valves to equalise pressures and to strip trapped or adsorbed gases from the solids.

3.3.5.4 Dust Separator for Exit Gases

It is usually necessary to recover the solids carried by the gas leaving the freeboard part of the fluidized bed. Generally high efficiency cyclones are the most

suitable equipment for cleaning the outlet gases. Filter bags are not suitable because they blind very easily if operated near the dew-point of the gases (however, they are sometimes used on small scale units.) If the cyclones are installed outside instead of within the fluidizing chamber, it is essential to lag them, and the gas ducts to a high standard and to make provision for preheating them before starting up the dryer. When the collected dust from the cyclone is fed directly back into the fluidized bed, it is necessary to seal the bottom of the cyclone so that the collection efficiency of the cyclone will not be impaired by the passage of appreciable quantities of gas up through the solids-discharge point. This is usually done by sealing this dip leg in the fluid bed.

Materials Suitable For Fluidised Beds

An overriding material property in deciding whether to consider fluidized bed drying is the drying curve; coupled with the specification for the dried product. The particles in a fluidised bed are thoroughly stirred by the fluidising gas and hence the residence time in any one compartment of a continuous dryer may be negligible for some of the particles, and the material leaving a compartment will contain some, only partly dried particles despite the intimate contact of drying gas with every particle. The superficial water will be evaporated in a few seconds. This process corresponds to the constant-rate drying period. Any material which has a very long falling-rate drying period is therefore unlikely to be suitable for continuous fluidized drying even though batch drying of such material is seldom likely to be economic.

Another point to consider is the uniformity of residual moisture in the dried product. For many purposes it is essential that the range of moisture distributions in small portions of dried material is small since otherwise caking of the product could occur on storage.

Once this point has been settled, the suitability of a particulate solid for fluidised drying is best determined by a small-scale experiment using a transport chamber of at least 120 mm diameter. The size of solid particles which can be fluidised varies greatly

from less than 1 micron to 6.35 cm. It is generally concluded that particles distributed in size between 65 mesh and 10 microns are best for smooth fluidization. Large particles cause instability and result in slugging or massive surges. Small particles (less than 10 micron) frequently, even though dry, act as if damp, forming agglomerates or fissures in the bed, or spouting.

The range of particle size is important. When a reasonably closely sized mixture is fluidised the insipⁱent fluidisation velocity is some mean of the individual values for each size, and observation confirms that, as soon as the actual gas velocity in the bed is reduced below some critical value, the coarse particles settle out whilst the rest remain fluidized. On the other hand, when the gas velocity through a widely sized material is slowly increased, entrainment of the smaller particles commences as soon as the gas velocity above the bed exceeds the terminal falling velocity. In practice, it is not possible to select a gas velocity which will avoid both segregation and entrainment of particles of the same density if the ratio of the largest to smallest diameters exceeds [8]. This ratio is smaller if the particles become even slightly porous on drying. Moreover a check must be made that particle size distribution does not change during the drying process; thus some particles tend to agglomerate when fluidised and some to disintegrate.

It also follows that wet material must be fed to the drying chamber without choking and that the dried material will run out smoothly.

3.3.6 Continuous Through-Circulation Dryers

Continuous through circulation dryers operate on the principle of blowing hot air through a permeable bed of wet material passing continuously through the dryer. Drying rates are high because of the large area of contact and short distance of travel for the internal moisture.

The most widely used type is the horizontal conveying screen dryer in which wet material is conveyed as a layer on a horizontal mesh screen or perforated apron, while heated air is blown either upward or downward through the bed of material. Alternative types include the solid band dryer where the material is dried by either

blowing hot gas over or down into the material or by heating the solid band.

The horizontal conveying screen dryer consists of a number of individual sections, complete with fan and heating coils, arranged in series to form a housing or tunnel through which the conveying screen travels.

The air circulates through the wet material and is reheated before reentering the bed. It is not uncommon to circulate the hot gas upward in the wet end and downward in the dry end. A portion of the air is exhausted continuously by one or two exhaust fans, suitably sized, which handle air from several sections. Since each section can be operated independently extremely flexible operation is possible, with high temperatures usually at the wet end, followed by lower temperatures. The maximum pressure drop that can be taken through the bed of solids without developing leaks or air by-passing is roughly 50 cm of water.

Through-circulation drying requires that the wet material be in a state of granular or pelleted subdivision so that hot air may be readily blown through it. Many wet materials reach dry materials such as centrifuge filter cakes can sometimes be granulated to give a suitable porous bed on the conveying screen. In a few cases powders have been pelleted or formed into briquettes to eliminate dustiness and permit drying by through-circulation.

Steam heated air is the usual transfer medium used in these dryers, although combustion gases may be used also. Conveyors may be made of wire mesh screen or perforated steel plate. The minimum practical screen opening size is about 20 mesh.

3.3.7 Rotary Dryers

A continuous rotary dryer is one in which the wet material is continuously lifted by the rotation of the dryer so that it falls through a current of hot air passing down the length of the dryer shell. The dryer is slightly inclined to the horizontal so that material gradually flows along the length of the shell. The length of the cylinder may range from four to more than ten times its diameter, which may vary from 30 cm to more than 3 m.

The air flow may be either co-current or counter-current.

The rotary dryer is one of the most widely used forms of continuous dryer. It is simple and reasonably versatile and, in consequence, it is suitable for drying a wide range of materials rapidly and at low cost when quantities are large. Thus dryers can be designed to provide drying times ranging from 5 to 60 minutes and solid handling capacities range from a few hundred kg to 200 tonnes/h.

Rotary dryers are ideally suited for drying free-flowing granular products requiring moderate drying times. The tumbling action of the dryer is beneficial, within limits, for all products since any semi-permeable crust on the surface of the particles (case hardening) is disrupted, thus allowing easier escape of moisture from within. Rotary dryers are quite suitable for heat sensitive materials provided that the restriction of drying temperature does not result in excessive drying time. They are not however suitable for the following applications; slurries, sludges, and very sticky material; and slow drying materials requiring more than one hour for drying. In addition there are limitations in handling friable dusty or light materials which could easily be carried away in the air stream: indirect dryers rather than direct dryers should be given consideration for such cases.

Continuous rotary dryers can be classified into three types, the cascading direct rotary dryer, the direct dryer with peripheral louvres for the hot air and the indirect dryer.

Except with small dryers it is essential to cool nearly every product with a stream of air in a rotary cooler, or in a fluidised bed cooler, since the heat content of a continuous discharge of 20-200 t/h leaving a dryer at 100 °C would be excessive. In general cooling to a temperature 20-30 °C above ambient is desirable.

Ancillaries include air heaters or other form of heating, efficient dust collectors and fans and a system of (belt) conveyors for the incoming and dried product.

The Cascading Direct Rotary Dryer

The dryer is mounted on a slope of about 1 in 40 to 1 in 20 (though co-current dryers may be nearly horizontal). Attached to the inside wall of the dryer cylinder are

continuous rows of lifters (flights).

As the dryer rotates these lifters pick up the material and it cascades through the air stream. These flights are usually offset every 60 cm to 2 m to ensure more continuous and uniform curtains of solids in the gas. Any material not held up in the lifters must remain as a rolling bed in the bottom of the dryer shell and thus effectively by-pass the drying operation. Maximum heat and moisture transfer is obtained when all of the material is in the process of falling in cascades. It is also important that the cascades or curtains of falling material should be carried well across the dryer in order to achieve the best possible contact with the air stream. Thus lifters give the curtain pattern. Spiral flights are usually provided in the first few feet at the feed end to accelerate forward flow from under the feedchute, and prevent leakage over the feed end retainer ring into the gas seals.

When co-current gas/solids flow is used, flight may be left out of the final few feet at the exit end to reduce entrainment of dry product in the exit gas. Showering of wet feed at the feed end of a counter-current dryer will on the other hand, frequently serve as an effective means for scrubbing dry entrained solids from the gas stream before it leaves the cylinder.

Co-current flow of gas and solids is essential when a large proportion of the moisture is to be evaporated during the early stages of drying, as it permits the use of high air temperature without unduly high product temperatures, and thus can be used for dry temperature sensitive materials. Since the air and solid temperatures converge toward each other at the exit, the temperature of the dried solids leaving the dryer is easily controlled to a maximum whilst still retaining the advantage of a high temperature difference in the early stages of drying. In the counter-current dryer the dry solid temperature tends toward that of the inlet air. Consequently counter-current operation is indicated whenever it is necessary to heat the solid to a relatively high temperature to complete the drying process.

The Louvred Dryer

A louvred dryer is one in which the drying air flows along channels formed by special shaped louvred plates and escapes through the louvres into the bed of solids. A valve plate ensures that the air flows only to those louvres which are actually beneath the bed of solid and the downward pointing overlapping plates which form the louvres ensure that no solid material enters the air channels. The louvres form an inner drum that is lightly tapered and the solids move down the slope by kiln action. A dam ring is formed at the exit end by a system of overlapping hinged blades. In normal operation a relatively deep bed occupying about 40% of the dryer volume is used, but the bed depth can be altered by changing the angle of the dam ring blades; in the extreme, the dryer can be emptied very rapidly. The air is drawn off through a number of high efficiency cyclones.

Because it is a cross flow heat exchanger, the exit solids temperature approaches the inlet air temperature, which may limit the maximum value of the inlet air temperature.

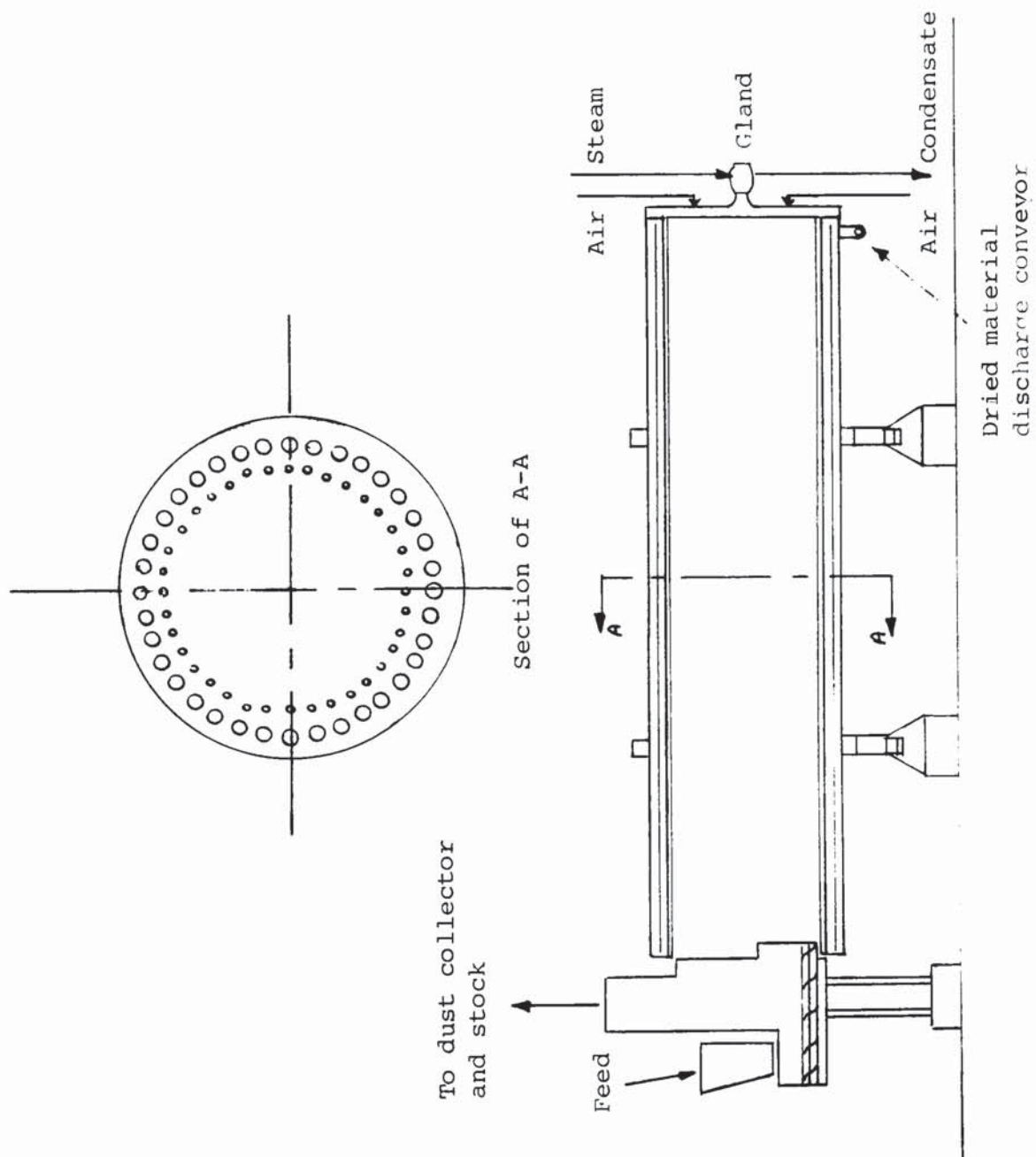
Since the air passes through the bed, the maximum air rate per unit area may be limited by fines carry-over and, in general, this dryer does not appear to be suitable for drying dusty material. Its best application appears to be to the drying of coarse dust-free material, where drying is mainly in the constant-rate region and with no severe restriction on the exits solid temperature.

The Indirect Dryer

One form of indirect dryer uses an inclined rotating shell as in the direct dryer, but the lifters are replaced by tubes containing steam or hot water. In small machines there is one row of tubes, but in most sizes two rows are employed, the inner row being of smaller diameter than the outer (see Fig 3.2). The feed is heated by direct contact with the tubes over which it flows in a thin layer. Air is drawn through the dryer in sufficient quantity to remove the water vapour. The air leaves the dryer almost saturated so that the

FIGURE 3.2

Diagram to show the principle of an indirect dryer
arranged for counter-current flow



quantity required is usually much less than in a direct rotary dryer. The problem of dust removal from the exit air is simplified and in many cases natural circulation without the use of fans is adequate. The air velocity is usually about 0.3 m/s.

The heating steam is introduced into the tubes, and the condensate is removed, through a rotary gland at the solid discharge end of the dryer. The dry solid is discharged through ports in the shell, which have dams to maintain a sufficient bed depth.

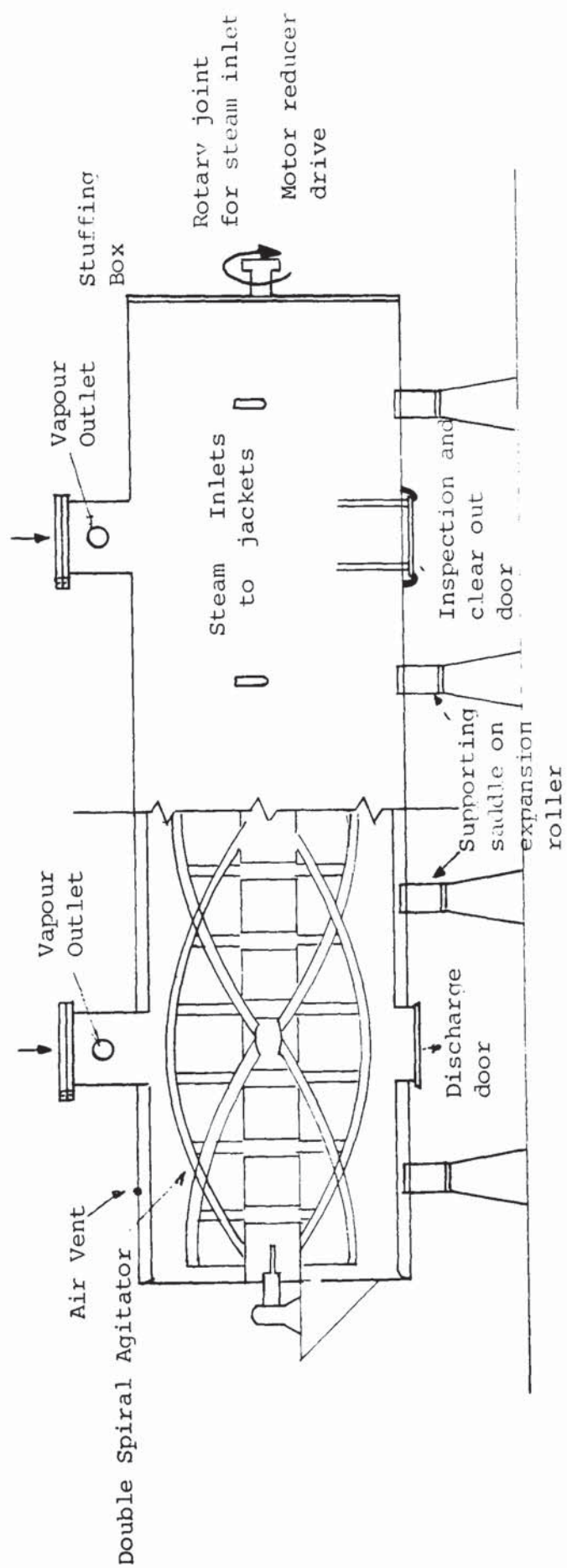
This dryer is especially suitable for materials with a long falling-rate period as it can hold them at a substantially constant temperature for a relatively long period, while the rolling action prevents caking and, by mixing the bed, facilitates escape of the water vapour. Because of the low heat losses in the exit air stream the efficiency is high. It is suitable for heat sensitive materials as the maximum temperature can be accurately controlled via the temperature of the heating medium. It is not suitable for any materials that cake strongly on the heating tubes. Indirect dryers cannot, for mechanical reasons, be as large as the largest direct dryers required for high throughputs but fortunately the outputs of material for which they are particularly suitable are relatively small. Plants have been supplied of diameters 1.5-3.0 m, 10-20m long. Typical diameters of the tubes are: outer row 110 mm, inner row 75 mm and a typical heat transfer rate is 2kw/m.

3.3.8 Vacuum Rotary Dryers

This is a batch type of rotary dryer. The more common type consists of a stationary cylindrical shell, mounted horizontally, in which a set of agitator blades mounted on a revolving central shaft stirs the solids being treated. Heat is supplied by circulation of hot water or steam or Dowtherm, through a jacket surrounding the shell and; in large units, through the hollow spiral or a double continuous spiral. The outer blades are set as close as possible to the wall without touching, usually leaving a gap of 0.32 cm to 0.64 cm. The dryer is charged through a port at the top and emptied through one or more discharge nozzles at the bottom, vacuum is applied and maintained by any of the conventional methods, ie steam jets, vacuum pumps etc., see figure 3.3.

FIGURE 3.3

Diagram of a typical vacuum rotary dryer



3.3.9 Pneumatic-Conveying Dryers

In the pneumatic-conveyor dryer the solid is dried whilst being transported in a stream of hot gas, usually air. The pneumatic conveyor dryer differs from the fluidised bed dryer in which the solid is also suspended in the air stream, in that the density of the suspension is much lower.

A pneumatic-conveyor consists of a long tube or duct carrying a gas at high velocity, a fan to propel the gas, a suitable feeder for addition and dispersion of particulate solids in the gas stream, and a cyclone collector or other separation equipment for final recovery of solids from the gas.

The solids feeder may be of any type; screw feeders, venturi sections, high speed grinders, dispersion mills, and puddle wheel slingers are employed. The selection of the correct feeder is essential, to obtain thorough initial dispersion of solids in the gas, and project the solids far enough into the tube to throw the feed vertically on the centre line of the drying tube. Large agglomerates are broken up while smaller ones are thrown up the tube where they rapidly disintegrate as they dry. The handling characteristics of the feed can be improved by recirculating a proportion of the dried product.

With larger dryers, two fans are employed so that the pressure differential is negligible at the feed point thus avoiding either blowout or infiltration.

Fans may be induced-draft or forced-draft type. The former is preferred usually because the system can be operated under a slight negative pressure. Dust and hot gas will not be blown out through any leaks in the equipment. Cyclone separators are preferred for low investment. If maximum recovery of dust is required, the cyclone may be followed by a wet scrubber or bag collector.

In a simple dryer of this type the residence time in the drying tube is in the region of 0.5-3.0 seconds so that only easily dried materials can be handled.

Most commercial dryers make some provision for recirculation of the feed in order to increase the average residence time up to about one minute. However, when recirculation is adopted there is no guarantee that each particle will go round the same

number of times, and there will be a spread of residence times about the nominal value. The higher the ratio of recirculation to throughput the greater will be the spread. Thus recirculation is not desirable if every particle should be given the same drying time.

Pneumatic conveyors are suitable for materials which are granular and free flowing when dispersed in the gas stream so they do not stick on the conveyor walls or agglomerate. Sticky materials such as filter cakes may be dispersed and partially dried by an air-swept disintegrator in many cases. Otherwise dry product may be recycled, mixed with fresh feed, and then the two dispersed together in the disintegrator.

The main requirement is that the operation must be instantaneous; internal diffusion of moisture must not be limiting in drying operations and particle size must be small enough so that the thermal conductivity of the solids does not control during heating and cooling operations. Pneumatic conveying can result in significant particle size reduction, particularly when handling crystalline or other friable materials. Pneumatic drying may be single stage or multi-stage depending upon the difficulty of drying the material.

3.3.10 Turbo Tray Dryers

The turbo-dryer is a continuous dryer consisting of a stack of rotating annular shelves in the centre of which tube-type fans revolve to circulate the air over the shelves. Wet material enters through the roof, falling onto the top shelf as it rotates beneath the feed opening. After completing one revolution, the material is wiped by a stationary wiper through radial slots onto the shelf below where it is spread into a uniform pile by a stationary leveler. The action is repeated on each shelf, with transfers occurring once each revolution. From the last shelf, material is discharged through the bottom of the dryer. The steel-frame housing, consists of removable insulated panels for access to the interior. All bearings and lubricated parts are exterior to the unit with the driers located under the housing. Parts in contact with the product may be of steel or a special alloy. The trays can be of any sheet material, such as enamelled steel, etc.

The rate at which each fan circulates air can be varied by changing the pitch of the fan blades. In final drying stages, in which diffusion controls or the product is light and powdery, the circulation rate is considerably lower than in the initial stage where high evaporation rates prevail. In the majority of applications air flows through the dryer upward in counterflow to the material. A separate cold-air supply fan is provided if the product is to be cooled before being discharged.

The turbo-tray dryer can handle materials from thick slurries to fine powders. It is not suitable for fibrous materials which mat, or doughy or tacky materials.

Heaters can be located in the space between the trays and the dryer housing where they are not in direct contact with the product, and high thermal efficiencies can be achieved by reheating the air within the dryer, steam is the usual heating medium.

3.3.11 Other dryers

Other dryers that were considered are the screw conveyor dryer and the vibrating conveyor dryer. However screw conveyor dryers are not widely used because they have a limited efficiency as dryers. And the vibrating dryer is principally a conveyor and secondly a dryer and its field of application is limited.

Dryers that were not considered suitable for drying melamine phosphate were "continuous sheeting" dryers because melamine phosphate cannot be formed into sheets; "cylinder and drum drying" because it is felt that melamine phosphate would not adhere to the metal surface (however this should be verified); "vacuum freezing" because this is usually applied to organics, solutions and rarely to suspensions (purpose being to freeze the excess water and then allow it to sublime under vacuum conditions, which for the case of melamine phosphate would make the task more laborious), and it is costly and time consuming; and finally drying with "infra-red" because it is very expensive.

Conclusions

As high temperatures may affect the drying of melamine phosphate, by

producing crust formations, temperatures in excess of 120 °C should not be used, and to prevent agglomeration of the solids during drying, constant agitation would be required. Both Indirect Dryers and Vacuum Rotary Dryers fulfill both of these requirements, and neither have large volumes of air passing through the drying vessel. Both would have to be experimented with to identify the most appropriate method.

3.4 Storage of the dried melamine phosphate

Once dry, the melamine phosphate must be stored in well sealed plastic or metal containers to prevent ingress of moisture.

CHAPTER FOUR
COATING PREPARATION

CHAPTER FOUR

COATING PREPARATION

4.1 Mastic Preparation

On a small scale using a mixture that includes 20% melamine phosphate, an average sample is made up to the formulation shown in Table 4.1. The melamine phosphate crystals are mixed with the Araldite resin before the Versamid is added. Mixing was normally carried out manually until, upon visual inspection a uniform mixture was obtained. It was found that if the Araldite and Versamid were first blended, the inclusion of melamine phosphate due to the high viscosity of the combined system was extremely difficult. This standard formulation has a viscosity of 953 poise at a shear rate of 2.3 sec⁻¹ found using the Haake viscometer. This sample was poured and scraped onto a flat 95 mm square fire test plate and was allowed to self-level forming a one coat system. The test plates resulted in a 5 mm thick coating covering an area of 0.01 m², corresponding to an average coverage rate of 6 kg/m². Self levelling took about 1-2 minutes indicating that application to a vertical surface may not be easy. At higher loadings of melamine phosphate the mixture viscosity had increased to such an extent that trowelling was necessary during mastic application.

Mixing large volumes of highly viscous material including both liquids and solids is highly complex, particularly for continuous processes. In batch mixing, a double motion paddle mixer would be suitable as shown in Fig 4.1. This is used extensively for mixing adhesives, greases and in baking; similar in many respects to the Kenwood major (shown in Plate 4.1) used for producing batches of mastic in this project. The anchor stirrer used ensured a well mixed product, though did tend to lead to a high degree of aeration; mixing by hand using a folding action reduced this considerably. Once mixed, the mastic must be applied to the designated surface before chemical reaction increases viscosity excessively.

PLATE 4.1
KENWOOD MAJOR MIXER USED IN SAMPLE PREPARATION



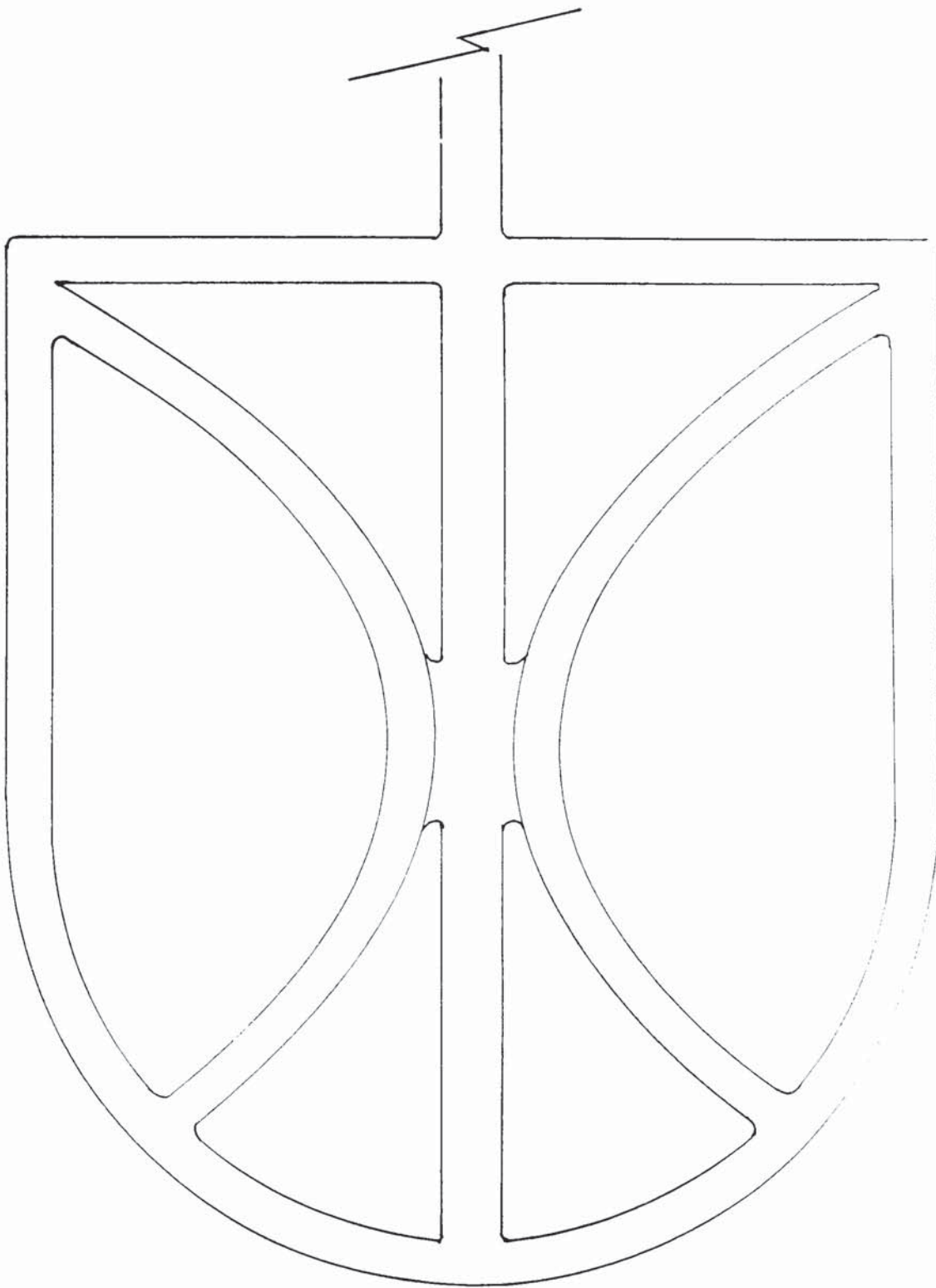
Table 4.1
Average sample containing 20% melamine phosphate all weights given in grams

	Araldite	Versamid	Melamine Phosphate
1 sample	43	18	12
5 sample	215	90	60
10 sample	430	180	120

Table 4.2
Reduction in solubility of melamine in melamine phosphate after heat treatment

Type of Melamine Phosphate	at 210°C Melamine Phosphate Dried at 110°C mole/litre	Melamine solubility Melamine Phosphate Treated for 48 hrs at 210°C mole/litre
Needles (C ₃ H ₆ N ₆) _{1.0} H ₃ PO ₄	0.022	0.0025
Small needles (C ₃ H ₆ N ₆) _{1.2} H ₃ PO ₄	0.023	-
Small block plates (C ₃ H ₆ N ₆) _{1.3} H ₃ PO ₄	0.023	0.0025
Thin reflective plates (C ₃ H ₆ N ₆) _{1.3} H ₃ PO ₄	0.015	0.0114
Block plates (C ₃ H ₆ N ₆) _{2.0} H ₃ PO ₄	0.014	0.0036

FIGURE 4.1 A double motion paddle mixer



A good adhesive bond between substrate and coating is very important; inadequate bonding will allow detachment before or during a fire. To fulfill this objective both the adhesives properties and the properties of the bonding surface must be carefully considered.

4.2 Surface Preparation

If corrosion products or other surface contaminants are not removed, failure of the coating may result through one or more the following mechanisms:

1. Simple mechanical interference with proper adhesive contact between coating and substrate will result in coating failure, if the contaminant loses adhesion to the substrate.
2. Absorption of moisture or corrosive chemicals by osmosis or by leaking through a crack followed by substrate corrosion and/or surface degradation.

The selection of the surface preparation method is dictated by the substrate-coating combination involved, an epoxy system is characterised by poor wettability, of steel surfaces and high cohesive strength and so tends to pull away from a poorly prepared surface.

The surface to which the coating is to be applied should be free of all grease and oil, as well as any adhering foreign matter, these could be removed using abrasive blasting, this involves directing abrasive particles, for example natural sand or flint, against a surface at high velocity. Many studies have demonstrated that application to a blasted surface greatly prolongs the life of maintenance coatings [16]. In fact it has been found that preparation by sandblasting increased life expectancy more than four times over that of steel surface that had been weathered and wire brushed before painting [17]. This surface, once clean, should be primed so as not to allow oxidation of the surface (and so produce a less adherent surface; a zinc based primer would be useful).

Zinc galvanised steel often present an adhesion problem and sandblasting for cleaning may cut through the zinc coating. Washing surfaces with hydrochloric acid,

vinegar or copper sulphate solutions have now largely been abandoned, solvent wiping with mineral spirits or naphtha is usually recommended to remove any oil, grease or ordinary dirt. Weathering is often recommended as the best surface preparation of galvanised steel, during weathering, the zinc reacts with the atmosphere to form a protective film which minimises further reactivity between the zinc and the coating. The manufacturers of Versamid recommend that aluminium alloy be pretreated by a chromate method, and rust is removed from steel using hydrochloric acid followed by an etch in an alkaline cleaning bath.

Once the three or more components have been mixed the mastic must be applied as soon as possible, the factors which determine the method of application are;

- a. Physical properties of the adhesive
- b. Shape and dimension of the bonding surface
- c. Existing production facilities available.

The viscous coat could either be applied by hand, trowelling on and levelling using a solvent wet float, or by spraying the mastic onto the surface, using a specially adapted spray.

A trowelled finish would not be suitable for intricate surfaces and would not give a smooth coat, over large areas it would be extremely difficult to get an even coat. A sprayed coat would have the advantage of not creating air pockets and have a large coverage rate, but the spray gun system would have a purge or clearing line into the system so when spraying is stopped the gun and lines can immediately be flushed clean. Very high pressures would be required due to the viscous nature of the mastic.

4.3 Surface appearance

The surface of a sprayed coating should be smooth with few air bubbles at the surface, peaks and valleys are not desirable as they would present a larger surface area to the weather. The consistent colour of the coating is a dark cream, and it may be desirable to coat this with a second non-intumescent coat, though while this may not improve fire

protection it may harm it, and care should therefore be taken that this finishing top coat would act as a protective coat against the weather, would prevent leaching of the melamine phosphate from the coating and would also allow for an infinitely variable colour scheme.

4.4 Heat treating melamine phosphate

The melamine phosphate contained in the mastic is one of the 'active' ingredients and as such is critical in the mastics make up, any leaching of this material would lead to reduced protection in the event of fire. There are various possible methods of reducing or preventing leaching, these are

- a) Encapsulation of the melamine phosphate in the resin.
- b) Creating an impervious layer to prevent washing of the surface by rain.
- c) Reducing the solubility of the melamine phosphate.

The first method, the encapsulating the melamine phosphate though reducing the likelihood of leaching, also quenched intumescence so was abandoned. Painting the surface with an impervious coat would be a relatively expensive method, and would have to be maintained, material characteristics would play an important part in choice of coating, no adverse reaction should take place between the two coats that might affect the fire protective characteristics of the mastic.

By reducing the solubility of the melamine phosphate, the effect of washing the surface (ie rain) would be minimal, one way of reducing the solubility is to dry the melamine phosphate at 110 °C and then heat treat it at 210 °C for 48 hours as suggested by Yeadon *et al* [14]. Results showing the reduction in solubilities [10] after heat treatment are as given in Table 4.2.

Of the samples heat treated, it was found that heat treatment of small block plates had no effect on fire protection, though there was a greater degree of intumescence, and a better char structure produced. While with small needles the degree of intumescence was reduced and the coating had a poorer insulation value.

Different heat treatment temperatures were investigated and the results shown below in Table 4.3.

4.5 Weathering

Once the coating has been applied it will probably be open to attack by the weather, rain, frosts and sun which can all affect the coating, and measures must be taken to protect the surface.

The most common form of attack is rain, if the rain finds some way of penetrating the coating it may leach away the active ingredients, in this case the melamine phosphate. The solubility of melamine phosphate was found to vary between 0.02-0.06 mol/litre [10] depending on the crystal type and melamine phosphate ratio. First it had to be assessed if the melamine phosphate could be leached from the mastic, this was tested in 2 ways.

- a. an accelerated weathering test, where samples were placed in heated water tank with the temperature maintained at 85 °C for 1 to 5 days. Each of the samples was placed in brass plates constructed to the same dimensions as the mild steel plates used normally.
- b. an outside weathering test carried out over 18 months, the sample being positioned where it is open to attack from rain, sun and frost.

Both samples had been previously cured as normal.

On completion of the first test (a) the samples were examined carefully. The colour of the samples had changed from pale yellow to a dark brown and visible pitting had taken place on the front face. The samples had also expanded and cracked, some samples obviously coming away from the sample plate though remaining in place. Each sample was well drained and then dried in a warm oven (50 °C) for 36 hours. The four samples made were then individually fire-tested.

At the start of each fire test the samples did not behave in the normal manner. Intumescent was less and a flammable tar produced in a similar fashion to the overcure mentioned in section 4.6.

Table 4.3

Heating Regime			Water Solubility at 100°C (g/100ml)	Moisture Absorption at 25°C % in 48 hrs
Temp. (°C)	Time (hrs)	Weight (%)		
120	16	-	4.5	5.8
200	5	5.6	1.0	4.9
210	5	5.6	1.0	2.8
220	5	7.6*	0.25	8.1
250	5	13.8	0.25	22.5
* MI ₃ evolved at these higher temperatures				

Char had the same insulating affect as any other char produced, any cracks formed due to the fierce weathering test adopted were soon filled and the sample once intumesced had good adhesion to the plate. Photographs of the pre tested accelerated weathered samples may be seen in Figure 4.2. The temperature/time plots for the fire test can be found in Figure 4.3.

After an eighteen month period [6] exposed to all weathers the two samples were examined. The colour of each of the samples had changed from yellow to a light beige colour and few visible cracks had formed. On fire testing little visible loss in intumescence was noticed, the only difference noticed was the char produced had fewer large voids, this compared quite well with one sample which had been left to cure (at room temperature for 14 months), and this explained the increased durability of the char and the improved insulation factor.

It was found then repeating test (a) that the fire tests results were repeatable, but the cracks and colour change were still evident, and it was concluded that the weathering tests had no effect on the intumescent characteristics of the coating. If any melamine phosphate was leached from the mastic, it was only from the surfaces exposed to water, and with improved surface treatment the coating may remain intact.

4.6 Curing

The standard cure used for samples was 24 hours at ambient temperature, followed by nine days at 55 °C. As curing takes place the large numbers of hydroxyl groups required for esterfication by phosphate are formed. This esterfication is the first stage in the reaction leading to intumescence.

A few hydroxyl groups are already present in oligomers of the diglycidylether of bis-phenol A as shown

FIGURE 4.2

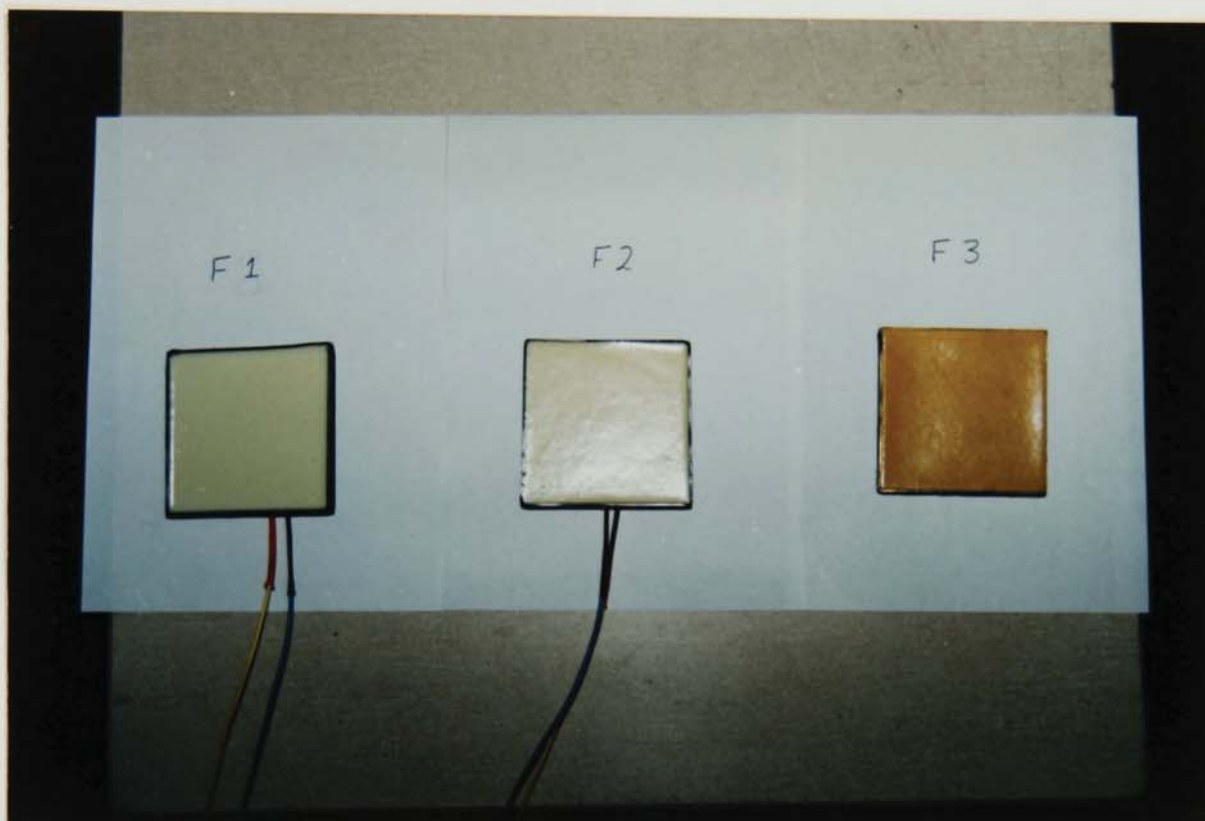
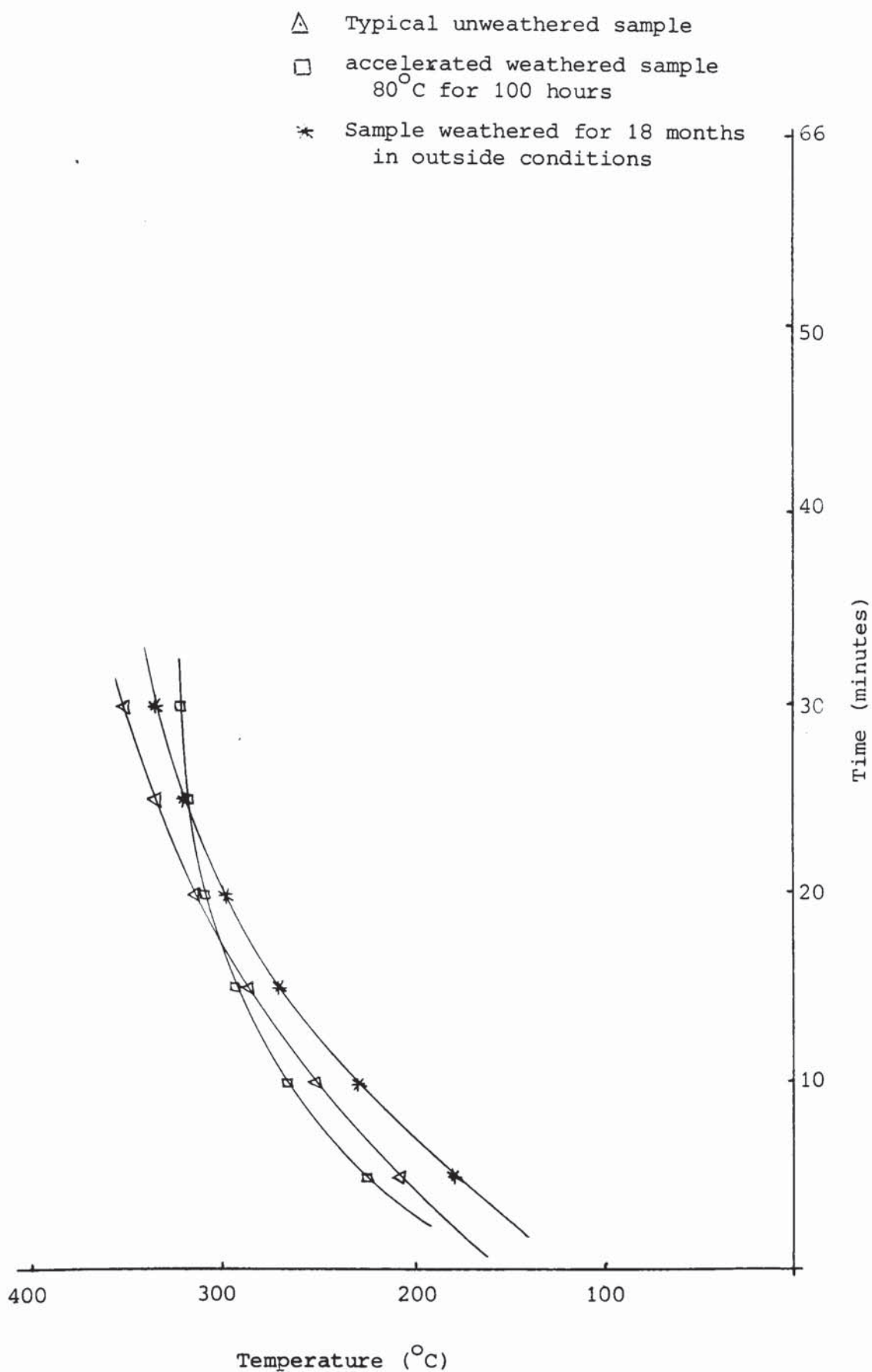


FIGURE 4.3

Fire tests weathered samples containing 30% small
needles melamine phosphate $(C_3H_6N_6)_{1.2}H_3PO_4$
Distance from burner 22cm



Methods of heat curing

1. Direct heat curing -
 - A. Oven circulatory type giving accurate temperature control
 - B. Liquid Baths - rapid heat transference by conduction (but also leads to leaching of water soluble materials)
 - C. Hot presses or plates - electrical resistance or steam providing the heat, though the latter may lead to leaching, and the former being successful for large areas.
2. Radiation curing - using infra-red heaters, producing an increase in the heat transference rate, exceeding that of oven heaters.
3. Electric heaters - a conducting strip of metal is embedded in the adhesive and acts as an internal heater, recent forms of graphite [2-7] (felts, yarns, woven fabrics and tapes) have been used, causing rapid heating and cooling. The advantages of such a method include.
 1. rapid attainment of curing temperature
 2. localised heating
 3. no need for ovens
4. Hifrequency di-electric heating or induction heating - This method is not suitable for large areas or thicknesses, it tends to be used mainly for joints, it depends on two surfaces having high frequency molecules vibrating and so producing heat.
5. Ultrasonic Activation - this is based on the transmission of mechanical vibrations from an ultrasonic transducer to the adhesive. Once more suitable for joints.

When samples are produced for small scale testing, the most economic and repeatable method is using a direct heat curing method, in particular an oven, on a larger

scale this is of course impractical so other methods were considered all of which are expensive. The three most suitable are

1. using infra-red radiant heaters where large areas can be heat cured at any time
2. building a temporary housing or balloon around a large piece of equipment on site and heating the interior, this is of course limited by other equipment.
3. wrapping joints/pipes/tanks in a heating cloth and so curing the mastic.

Consideration of these methods shows heater operation for as short a period as possible would be the most economically desirable, so different time/temperature profiles were investigated.

Versamid 125: Epoxy resin adhesives will cure at ambient temperature, but cure time can be reduced by heating to elevated temperatures, certain examples being [12],

TABLE 4.4

Cure temp (°C)	Time for full cure in minutes
149	10
121	30
93	45
66	120

Where the Versamid 125: epoxy resin is 35:65 parts by weight.

Using this information a sample could either cure at ambient temperature or if 'intermediate' curing was required a high temperature cure could be considered. Various time/temp profile results are shown in Table 4.4 and it can be seen at high temperature cures (95 °C) an 'overcure' can take place.

In the samples are cured at 95 °C, a flammable tar was produced. On fire testing these samples, the 'cured' mastic burnt vigorously and this was a sign of an 'overcure'.

Tests to assess full cure

Cray Valley Products who distribute the Versamid 125 in Britain recommend three tests to assess full cure, these are:

1. **Extraction.**

A weighed cured sample is immersed in a solvent, for example acetone, which leads to all solubles being extracted. Analysis is then necessary.

2. **Hardness Development.**

Consecutive hardness test giving the same results indicate a complete cure, these tests should be carried out under the same conditions and over relevant periods of time, for example for a room temperature cure, the tests should be carried out daily after the first 10 days, in a higher temperature cure the hardness should be repeated every 6 hours after the first 24 hours.

3. **Swab Test.**

A swab soaked in MEK ketone should be contacted with the cured surface for 1 minute. The manufacturer considered 2-3 weeks at room temperature (15-25 °C) sufficient to fully cure a sample.

CHAPTER FIVE

MODIFIED FORMULATIONS

CHAPTER FIVE

MODIFIED FORMULATIONS

When considering modifying the formulation used, two different sets of characteristics must be examined. Firstly, those which affect the mixing and application of an uncur.ed mastic, and secondly, those that enhance the finished char. Each of course, may influence the other. It was found during preliminary investigations that:

- a) the mastic was difficult to mix and apply
- b) once applied the mastic had a tendency to flow off a vertical surface
- c) when exposed to fire, the char produced was too often friable, and under examination was uneven in texture.

The factors were examined experimentally and means of correcting or improving them were identified, as shown in the following sections. Firstly the best formulation producing the most durable and insulating char was chosen by using different types of melamine phosphate in different percentages in the mastic. Then the rheology of the system from the point of view of mixing and mastic application was examined. Finally, the effect of selected additives on mastic performance was considered.

5.1 THIXOTROPIC ADDITIVES

I RHEOLOGY MODIFICATION

Thixotropy pseudoplasticity, false body and shear thinning all describe a system which undergoes a viscosity reduction when subjected to shearing action. However rheologists use thixotropy to describe materials that have reduced viscosity for a measureable length of time after shearing action ceases, the latter three terms

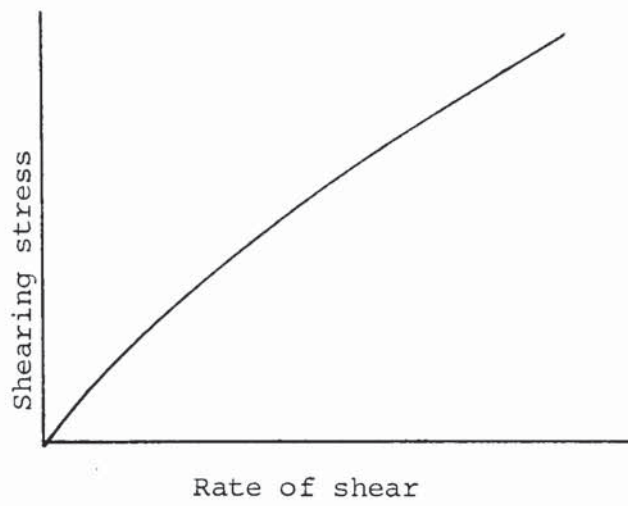
describe materials that exhibit reduced viscosity while subject to shear, but they immediately revert to their original consistency. All require a shear force before any flow can take place, and therefore the viscosity at zero shear rate is infinity, and materials act as solids until a shear force large enough to produce flow is applied. However a decreasing viscosity as shear rate ^{constant} ~~remains~~ is a unique thixotropic property. The change in viscosity as a function of shear rate for a false body material is the same for both increasing and decreasing shear rates.

The fluids described above are non-Newtonian fluids, ie where a plot of the shear stress S against shear rate n on cartesian co-ordinates is not a straight line, where plots of S and n are experimentally determined using a viscometer. The term viscosity has no meaning for a non-Newtonian fluid unless it is related to a particular shear rate n , as apparent viscosity μ_a can be defined as follows

$$\mu_a = \frac{S}{n} \quad \dots 5.1$$

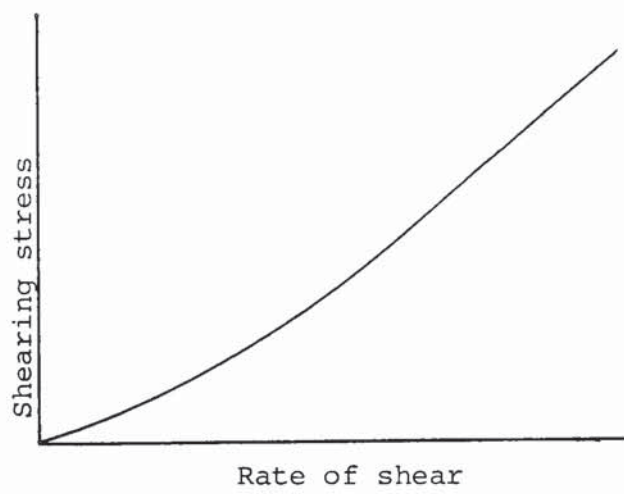
When the apparent viscosity μ_a decreases with an increase in shear rate n as shown in Fig 5.1 the fluid is said to be pseudoplastic. When μ_a increases with an increase in n as in Fig 5.2 the fluid is said to be dilatant. Both pseudoplastics and dilatants are examples of time independent non-newtonian fluids, ie the apparent viscosity depends only on the rate of shear at any particular moment and not on the time for which the shear rate is applied.

Fig 5.1



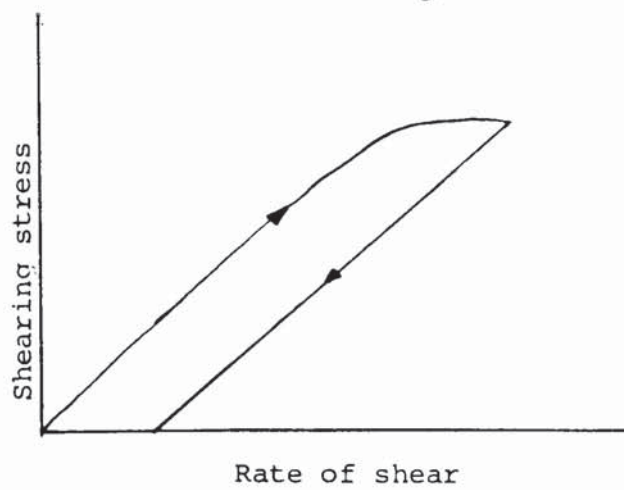
Pseudo plastic

Fig 5.2



Dilatant

Fig 5.3



Hysteresis
affect

The class of fluids whose apparent viscosity continues to change as a function of time are known as time dependent non-Newtonian materials. Fluids which become more pseudoplastic with time at a constant shear rate are known as thixotropic fluids. Their structure progressively breaks down with time at a constant shear rate. Thixotropy is a reversible process. Eventually, a dynamic equilibrium is reached where the rate of structural breakdown is balanced by the simultaneous rate of reformation. Thus a minimum value of the apparent viscosity is reached at any constant rate of shear. Most thixotropic fluids will recover their original viscosity if allowed to stand for a sufficient length of time, some fluids will revert almost immediately while others might take several hours.

A plot of shear stress S against shear rate n for thixotropic fluids, as in Fig 5.3, shows a hysteresis effect when the shear rate is changed at regular time intervals. The curve obtained for increasing shear rates does not coincide with the curve for decreasing shear rates.

Fluids which become more dilatant with time at a constant shear rate are known as rheopectic fluids. Small shearing motions facilitate the formation of structure. Above a critical point, breakdown occurs. If the shearing rate is rapid, the structure does not form. In general, the apparent viscosity of rheopectic fluids increases with time to a maximum value at a constant rate of shear. Most rheopectic fluids revert very quickly to their original viscosity if left to stand.

For non Newtonian fluids the relationship between n and S is complex, and for time independent fluids can be written as

$$n = f(S) \quad \dots 5.2$$

In terms of velocity in the horizontal x direction, the above equation (5.2) can be written for a point in the z direction in the form

$$\frac{-dV_x}{dx} = f(S_{zx}) \quad \dots 5.3$$

for a point in the radial r direction in the form

$$\frac{-dV_x}{dr} = f(S_{rx}) \quad \dots 5.4$$

Equations 5.2, 5.3 and 5.4 are general equations for time independent fluids in which the function relating the shear stress and the shear rate is undefined.

Attempts have been made to define this function by formulating mathematical models to represent the rheological behaviour of non-Newtonian fluids. The simplest and most commonly used relationship is the power law equation,

$$S = K (\dot{\gamma})^a \quad \dots 5.5$$

where K is called the consistency coefficient and a the power law index. Fluids which obey the above equation are called power law fluids.

For pseudoplastic fluids $a < 1$, for dilatants $a > 1$ and in the case of Newtonian fluids $a = 1$ and K becomes the coefficient of dynamic viscosity μ .

$$S_{zx} = -K \left(\frac{-dV_x}{dz} \right)^{(a-1)} \frac{dV_x}{dz} \quad \dots 5.6$$

$$S_{rx} = -K \left(\frac{-dV_x}{dr} \right)^{(a-1)} \frac{dV_x}{dr} \quad \dots 5.7$$

Equation 5.6 and 5.7 represent equation 5.5 in the z direction and radial r direction respectively.

Other mathematical models for time independent non-Newtonian fluids are

Eyring, Ellis and Beiner-Philpoff models [23]. The Eyring model is a two-parameter model which can be written in the form,

$$S_{zx} = A \operatorname{arc} \sinh \left(\frac{-1}{B} \frac{dV_x}{dt} \right) \quad \dots \quad 5.8$$

The Ellis is a three-parameter model which can be written in the form

$$-\frac{dV_x}{dz} = \left[A + B (S_{zx})^{m-1} \right] S_{zx} \quad \dots \quad 5.9$$

The Reiner-Philpott model is also a three parameter model. It can be written in the form

$$-\frac{dV_x}{dz} = \frac{S_{zx}}{A + \frac{(B-A)}{1 + (S_{zx}/c)^2}} \quad \dots \quad 5.10$$

All these rheological mathematical models are empirical curve fitting equations, and as such are only reliable when used within the range of available data.

5.2 PROPERTIES OF THIXOTROPIC ADDITIVES

Many materials may impart thixotropic properties to a mixture, choosing the right one to suit the system depends on the exact properties required. In the epoxy system used, the coating produced must be either brushable or sprayable, and so under shear the viscosity must be low enough to allow this, but once on the coated surface, must not sag/run off so the viscosity must return to normal rapidly. If a pseudoplastic additive was used the viscosity would regenerate too rapidly and not allow brush marks to flow and level while a thixotropic material would remain at a reduced consistency for a short time; short enough to prevent excessive flow and

sagging.

Types of Thixotropic Agents

1. The most common thixotropic additives are the highly adsorptive silicas, where the particle structure resembles a sponge. Where more false body than thixotropy is required, and clarity is not required the most economic modifier would be diatomaceous silica; where good clarity or thixotropy is of importance pyrogenic silica or silica aerogel would be the correct choice. Once more the sponge like structure of the particle provides a high surface area and absorptivity, so that 2.5% is sufficient to impart significant resistance to flow in an epoxy resin.
2. Other filler materials such as mica, talc and china clay may impart some thixotropy, but their prime function is that of a filler.
3. A second class of thixotropic material is mineral inorganic, this includes bentonite clays treated with fatty quaternary ammonium chloride compounds, and metallic soaps, such as aluminium stearate, zinc stearate and lead stearate. These materials produce gels that are more false bodied than thixotropic.
4. Relatively pure organic materials, including thermoplastic polyamide resins and hydrogenated castor oils as well as a number of derivatives of hydrogenated castor oil. The two latter compounds are usually marketed as proprietary additives and very little is revealed of their chemical make-up or the method by which they function. Used primarily to provide sag resistance in coatings and incorporated as part of the pigment dispensing separation.

More has been revealed about the use of polyamides as thixotropic agents,

many of the techniques and the chemical background are revealed in US Patent 2.663.649 and 2.861.048. They are the only transparent thixotropic modifiers, but their gels have more false body than thixotropic properties.

Choice of Thixotropic Agent

Fumed silica is one of the most widely used thixotropic agents, and is already used with much success in epoxy resin systems. The two brand names of fumed silica used were Cabosil¹ and Aerosil², and within these two brands are various grades of fumed silica having different properties, those for Cabosil are shown below in Table 5.1. The grades vary with respect to surface area, particle diameter, and degree of compression. Certain grades are recommend for any particular application/use.

Grades with a larger surface area, in general, produce higher levels of thickening and thixotropy at a given concentration, but will require more dispersion energy to obtain the greatest benefit from their extra thickening capability. If not sufficiently dispersed all exhibit an efficiency that appears to be only equal to that of completely dispersed lower efficiency grades.

Incorporation of the Fumed Silica

The efficiency of a filler or thixotropic agent greatly depends upon their dispersion. For example, with fumed silica in a non-polar system the better the dispersion the higher the viscosity and thixotropy, whereas in a polar system, intense dispersion of the silica results in a viscosity decrease. Here large particle chains become separated and strongly solvated; relinking of the silica particles to form longer chains is impossible after solvation. Solvation can also occur in underdispersed systems, but is delayed. Thickening initially is pronounced, upon ageing of the system, however, viscosity decreases, this has been shown to happen in an

¹ Manufactured by Cabot Carbon Ltd

² Manufactured by Degussa

Table 5.1**Recommended additives classified by commercial applications**

Application	Function of Cab.O.Sil	Grade of Cab.O.Sil	System Class¹	Recommended Additives	Comments
Epoxies	Thickening Thixotropy	M-5 EH-5	11-A and 11-B	Thicken W/glycerine Thicken W/Anionics (Ultrawet 45KX) Thin W/Nonionics (Low HLB)	
Paints (Alkyd)	Thickening Anti-Sag Anti-Settling Thixotropy TiO ₂ Extension Gloss reduction	M-5 M-5, MS-7 MS-7	11-A and 11-B	Thicken W/ethylene glycol or W/Anionics (Ultrawet 45KX) Thin W/Cationics (Adogen 572) (Duomeen TDO)	Leveling and penetrating, May slowdown drying process of alkyd.
Paints (Latex)	Thickening Anti-Sag Gloss reduction	M-5 MS-7	1	Thicken W/Nonionics (Metallic driers) (Triton X-100) or with Cationics (Adogen 572)	
Varnishes (Alkyd)	Gloss reduction	MS-7	11	Thicken W/Nonionics (Metallic driers) (Tween 20) Thin W/Cationics (Adogen 572)	May slow down drying process of alkyd.

- ¹ I - Highly hydrogen-bonding
II - Medium hydrogen-bonding
III - Non-hydrogen-bonding

Shear stress $\tau = \dots$
 Schergeschw. $D = \dots$
 Shear rate
 Viskosität $\eta = \dots$
 Viscosity



Datum
Date
Nr.
No.
Substanz
Substance
Temperatur
Temperature

ROTOVISCO RV

Meßkopf
Measuring head
Meßeinrichtung
Sensor system

Faktor A
Factor

Faktor M
Factor

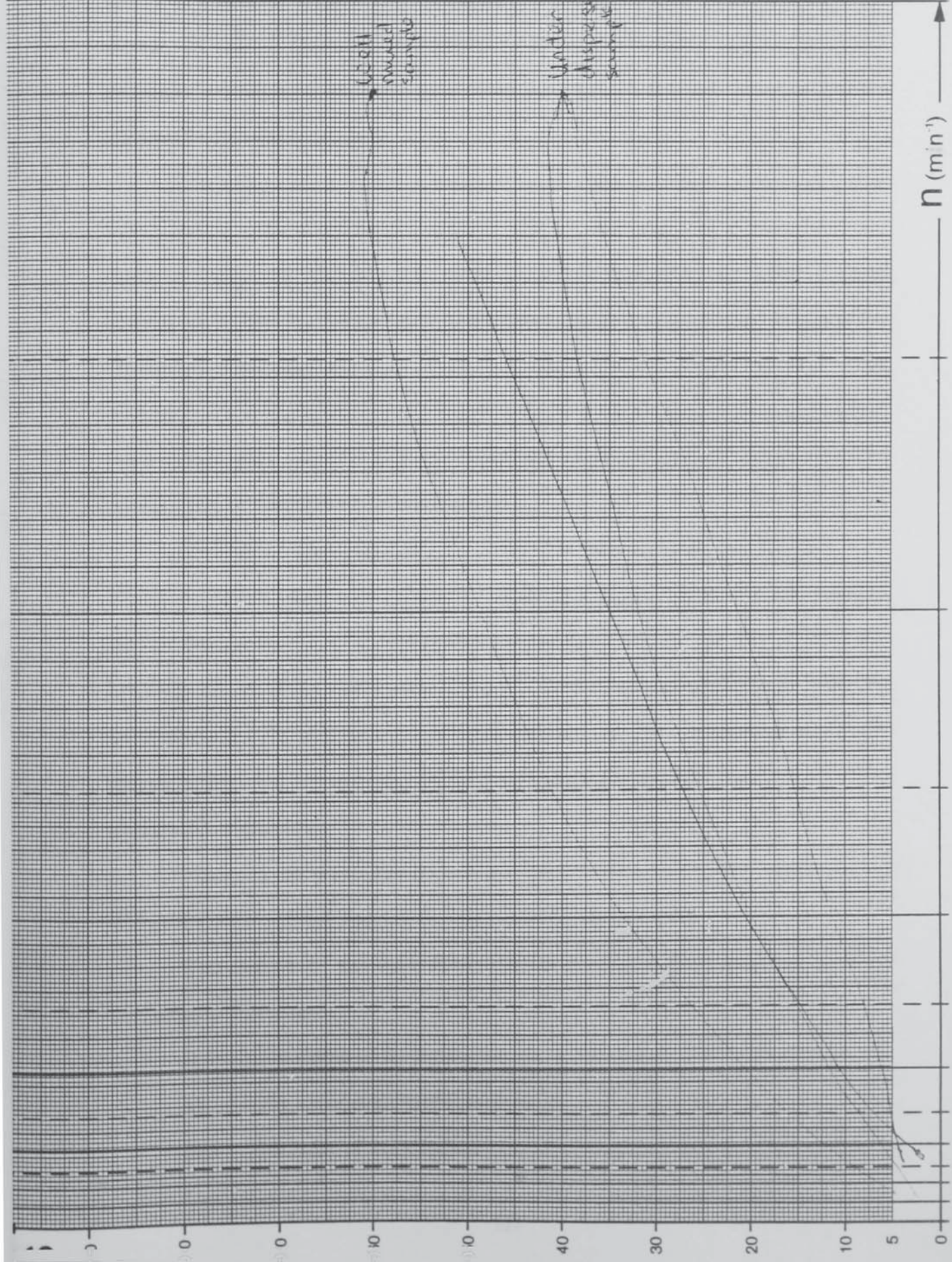
Faktor G
Factor

Programm
Program

Unterschrift
Signature

Bemerkungen:
Remarks:

Figure 5.14
 A sample containing
 26% melamine resin
 3% Celvol and
 71% ...



undermixed Cabosil/Melamine phosphate/Araldite/Versamid system, see Fig 5.4, excessive work or over dispersion causes a pronounced decrease in the systems viscosity, this is irreversible and cannot be compensated for by allowing the system to rest. It results from the attachment of hydrogen-bonding substances to the available hydroxyls on the fragments of the fumed silica network, preventing them from rejoining with each other.

When dispensing higher concentrations of silica in a small quantity of liquid with subsequent thinning (master-batch technique), it is important to select the right viscosity range by varying the Aerosil/Cabosil concentration. The highest concentration does not always result in the best dispersion. As a general rule, optimal dispersion of the silica particles is not obtained in systems of high viscosity when diluting concentrated batches. It is important to add the unfilled portion to the silica paste rather than visa versa, as the optimum dispersion of the Aerosil/Cabosil particles can be deteriorated by the diluent.

Generally, viscosity and thixotropy of various systems increase with increasing fumed silica concentrations. Again this increase is more pronounced in liquids incapable of hydrogen bonding than in polar liquids capable of hydrogen bonding. In the latter system the fumed silica has a greater tendency to hydrogen bond than any other substance present in the system, the hydroxyl groups attached to the silica have no competition from other substances in their hydrogen-bonding attraction for each other.

Viscosity increase and thixotropy development are direct results of the Cabosil/Aerosil network formation, through hydrogen bonding.

The degree of network formation in a formulation depends on eight parameters. These are:

- i) The nature of the liquid
- ii) The concentration of fumed silica
- iii) the grade of fumed silica

- iv) Degree of dispersion
- v) The pH of the system (if aqueous)
- vi) The temperature of the system
- vii) The degree of aging of the system
- viii) The nature of the other minor ingredients of the system, commonly grouped under the general term additives.

Network formation produces an increase in the viscosity of the system whenever it is at rest. When the network is temporarily fragmented during shearing action, the real and apparent viscosities decrease in proportion to increased speed of shear rate or length of time at constant speed. Upon the cessation of shear force, the viscosity approaches its original value - and again this is achieved efficiently because the fumed silica has no competition for its own bonding sites. Concentrations of 2-5% fumed silica by weight are usually sufficient to provide gel formation in non-hydrogen-bonding systems, smaller concentrations will provide any viscosity required up to the stage of gelation.

High hydrogen-bonding systems diminish the capability of fumed silica aggregates to link with each other. In this type of system there is competition from the liquid molecules for the fumed silica hydroxyls - so that the statistical probability of silica-to-silicate bonds is reduced. Instead, chain-termination caused by hydrogen bonding of solvent molecules to the fumed silica aggregate surfaces will be a significant factor - with large concentrations of fumed silica required to produce a given increase in viscosity and thixotropy. Concentrations of up to 10% are required to create gelation.

Methods of Dispersion

Various methods have been investigated and reported by a producer of fumed silica, Degussa [25].

It was found that a blade or propeller stirrer caused an incompletely thickened

or thixotropized mixture, whereas a 'dissolver' improved the dispersion possible, the dispersion intensity being primarily a function of the circumferential speed of the 'dissolver' disk, and depends only to a slight degree on the duration of dispersion. A greater degree of dispersion, and hence lower viscosity values were obtained when a roller mill was used. In a ball mill a concentration of about 6% fumed silica and a dispersion time of about 48 hours gave good results.

Dispersion of a 6% paste in a kneader produced better results than that produced with a stirrer, as did a 2.5% mixture produced in a pearl mill (diluting a 6% kneaded mixture to 2.5% before feeding into the pearl mill).

Good dispersion was also achieved using ultrasonic dispersion equipment (sonalators), having first predispersed the fumed silica using a high speed stirrer. If the latter is not carried out, a single passage through a one-nozzle sonolator is not sufficient for optimum dispersion.

Testing various methods of dispersion in the laboratory on a small scale, it was found that the best and easiest way of including the Cabosil was to first thoroughly mix it with the Melamine Phosphate, then add the Araldite and mix, and finally include the Versamid. All mixing for single samples was carried out by hand, though when mixing larger batches the rotary mixer (Kenwood Major) was used, both produced similar samples.

Other methods of inclusion were

1. Mixing the Melamine Phosphate, Araldite and Versamid together and adding the Cabosil,
2. Adding all four ingredients together and mixing,
3. Mixing the Melamine Phosphate and Versamid and the Cabosil and Araldite separately, then combining the two mixtures.

In each case it was found that due to the low density of the cabosil mixing was extremely difficult.

Production of Fumed Silica

Pyrogenic or fumed silica may be produced in four ways:

1. Silica (usually sand) can be vaporised at +2000 °C. On cooling anhydrous amorphous silica particles form. In the presence of reducing agents, eg coke, silica, sublimates at about 1500 °C to produce SiO, which can then be oxidised to form particulate SiO₂.
2. Oxidation of silicon tetrachloride vapour at high temperature produces SiO₂ + Cl₂.
3. SiCl₄ burned with methane or hydrogen at 1000 °C - 1800 °C to produce SiO₂H₂O and HCl gas, this is an important commercial process producing a narrow particle size distribution.
i.) $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ ii.) $\text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2\downarrow + 4\text{HCl}\uparrow$
4. Silicon ester vapours can be oxidised and hydrolyzed to form particulate silica of high purity (at high cost).

Pyrogenic Silica is extremely pure (SiO₂) prepared from high temperature reactions. It is amorphous to X-rays and does not cause silicosis, although excessive inhalation should be avoided. Pyrogenic silica particles have surface silanol (= SiOH) groups and internal Si-O-Si bonds. The silanol groups determine the silicas physical and chemical properties. The particle size varies from 3-10 nm with a surface area of 50-380 m²/g. It gained its name 'fumed' silica because of its smoke like appearance as it forms the flame. The term 'pyrogenic' silica has been discontinued because of the ambiguity resulting from other common definitions of the word pyrogenic, ie 'flammable' and 'fever-producing', it has neither of these properties.

Surface Chemistry of Fumed Silica

During the formation of fumed silica, hydroxyl groups become attached to

some of the silicon atoms on the particle surface. Thus producing a hydrophilic surface capable of hydrogen bonding with suitable molecules of materials in vapour, liquid or solid form. It absorbs moisture from the surrounding atmosphere/materials (greater absorption with larger surface areas) and it is this which makes it an excellent free flow agent for lumpy or hygroscopic solids. The moisture adsorbed on the surface of the fumed silica can be removed by evacuation at room temperature or by heating at 100 °C.

It has been shown by an infra red spectrum of fumed silica that there are at least two different types of hydroxyl groups. On the surface, in fact three groups can be identified, these being

- i) the isolated hydroxyl group
- ii) hydrogen-bonded hydroxyl groups
- iii) the siloxane group

(shown in Fig 5.5)

The isolated hydroxyl groups attached to the surface silicon atom, surrounded by siloxane groups (Si-O-Si) are hydrophilic. Hydrogen bonded hydroxyl groups, resulting from the presence of hydroxyl groups attached to neighbouring surface silicon atoms, are also hydrophilic. The siloxane group is non-polar and accounts for the hydrophobic characteristics of that part of the silica surface. At 110 °C dehydration occurs, shown in Fig 5.6, this may be reversed by exposure to air at 100% relative humidity or by immersion in water. At temperatures in excess of 800 °C the fumed silica starts to sinter with a consequent loss in surface area, this is irreversible.

The surface hydroxyl groups are capable of forming hydrogen bonds between fumed silica aggregates, hence with large enough concentrations producing network formations. This depends on the degree of dispersion, and on its ability to form chains through hydrogen bonding.

FIGURE 5.5

Typical groups which can occur on the Cab-O-Sil aggregate, determining its surface chemistry

Siloxane
groups

Isolated
hydroxyls

Hydrogen-Bonded
hydroxyls

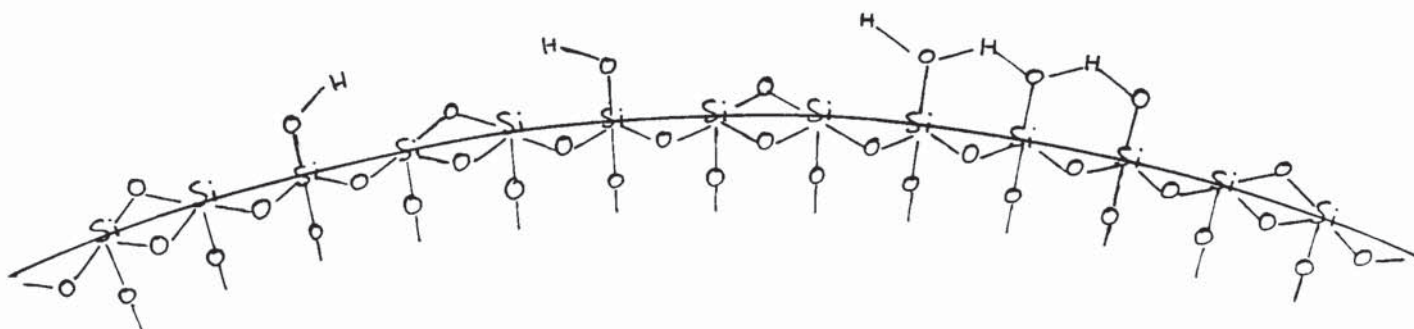
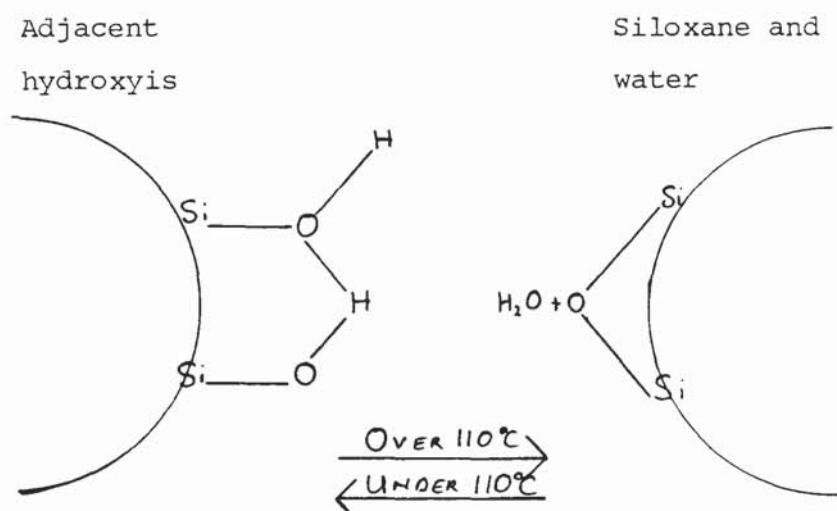


FIGURE 5.6

Reversible dehydration of the Cab-O-Sil surface



Other advantageous effects of Fumed Silica

a) Fumed Silica for Suspensions

Fumed silica can act as a suspension agent, sometimes called an 'anti-settling' agent, the suspending action being a result of three distinct properties or functions.

Firstly the extremely small particle size makes it unlikely that the silica particle itself will settle.

Secondly the fumed silica thickens the system, and any increase in the viscosity of a system reduces the probability that suspended particles will settle.

Thirdly, the lattice network of fumed silica in a liquid mixture ensures that suspended solid particles are isolated from each other, thus agglomeration into units too large to be suspended is minimised. Even during shear the lattice network breaks and reforms so quickly that agglomeration cannot take place.

The suspending ability of fumed silica is a function of the degree of chain formation in the system, and hence polar systems require more than non polar systems. It has been suggested for 100% epoxy resin systems 3-4% fumed silica is sufficient, though for application onto inclined surfaces, as much as 6% may be required. In cured samples of mastic containing 2% silica, a significant effect was noted: in cut samples no, or very little, solid build up was evident at the bottom of the sample and there were fewer air bubbles trapped in the solid.

b) Fumed Silica for gloss reduction

Gloss reduction or flatting is a property that can be imparted by fumed silica to a surface coating giving a hard rubbed finish, it is a permanent effect and not marred by subsequent ageing or development of white areas after drying.

c) Fumed Silica for anti-slip

Due to the micro-roughness of the Cabosil the coating once applied has less tendency to slip from the surface.

d) Insulation effects of fumed Silica in intumescent coating

Once incorporated in a coating the silica network helps to prevent excessive intumescence, and also acts to a certain extent as an insulator [21]. This was found to be true in work carried out by E Ball [26], intumescence was reduced, yet the insulation effect was increased.

Effect of Cabosil on the physical properties of the mastic

A sample containing no Cabosil was compared to samples containing different percentages of Cabosil (1%-5%) and various effects noted:

- i) Aesthetic effect;
- ii) Visual physical properties of the cured mastic;
- ii) Viscosity effects.

i) **Aesthetic Appearance**

Gloss/Colour of Cured Surface

Two samples cured under the same conditions, did exhibit noticeable differences. Firstly, in the dullness of surface created by the inclusion of the Cabosil, this did not appear to vary with the percentage used. When no Cabosil was used the surface was to a small degree glossy, once Cabosil was included there was a completely matt finish to the surface, the surface appeared to be very uniform.

Secondly the colour of the mastic system was lightened by the Cabosil, though it was not a great change due to the low percentages used.

ii) **Visual Physical Properties of the cured mastic**

The cured mastic had a larger number of bubbles when Cabosil was present, these being greater when larger percentages of Cabosil were used, this was thought to be due to the higher viscosity of the mixed mastic leading to more trapped air. This

Table 5.2

Viscosity of samples containing different percentages of Cabosit at different shear rates under equilibrium conditions.

(Digital read out ten minutes settle time)

		% CABOSIL			
		0	1	2	3
n (R.P.M.)	8	83,700	84,800	84,500	86,000
	64	87,400	79,100	65,400	53,200
	128	95,300	86,400	57,100	31,700

Viscosity in m Pa S.

was noticeable both on the surface of the cured sample, and from a cross-section of the sample. This is ⁱⁿ complete contradiction to the effect that Cabosil should have.

No great improvement could be found in the effect Cabosil had on suspended solids, no noticeable settling had been noted in the sample containing no Cabosil.

iii) Viscosity effects

Using a Haake Viscometer, Rotovisco Rv, the mastics behaviour under various shear rates was investigated. The Rotovisco system offers the versatility required to meet special rheological problems. It features 40 fixed rotor speeds and a speed range from 1 to 512 rpm. The choice of measuring heads having maximum torque values of 1.5 to 15N.cm and so allows the instrument to measure both very low and very high viscosity samples.

Due to the high viscosity of the mastic system, and the problem of removal and cleaning of any instruments, a cone and plate system was used. The head chosen was referred to as a Pk11 with a recommended viscosity range of 400-10⁵ mPa.s, and angle of 0.5°, and a radius of 10 mm. A Haake xy-t-recorder mapped out the responses which were then analysed.

The standard formulation containing 20% melamine phosphate and the Araldite and Versamid in a ratio of 5:2 was first assessed using the cone and plate system, and the viscosity of the system found to be 953 poise at a shear rate of 2.3 sec⁻¹ using Figure 5.7 and Appendix I (Method of calculating the viscosity from the curve produced).

It can be seen that a sample containing no thixotropic additives, does exhibit a hysteresis affect, it is a non-newtonian fluid. On addition of a thixotropic additive the affect becomes more pronounced, the higher the percentage of cabosil added the greater the difference. See Table 5.2 for the viscosities at different shear rates in samples containing different percentages of cabosil. It can be seen that the immediate effect of adding cabosil is an increase in viscosity. This clearly worsens the handling

Scherspannung $\tau = A$
 Shear stress
 Schergeschw. $D = N$
 Shear rate
 Viskosität $\eta = \frac{\tau}{D}$
 Viscosity



Datum
Date

Nr.
No.

Substanz
Substance

Temperatur
Temperature

ROTOVISCO RV

Meßkopf
Measuring head

Meßeinrichtung
Sensor system

Faktor A
Factor

Faktor M
Factor

Faktor G
Factor

Programm
Program

Unterschrift
Signature

Bemerkungen:
Remarks:

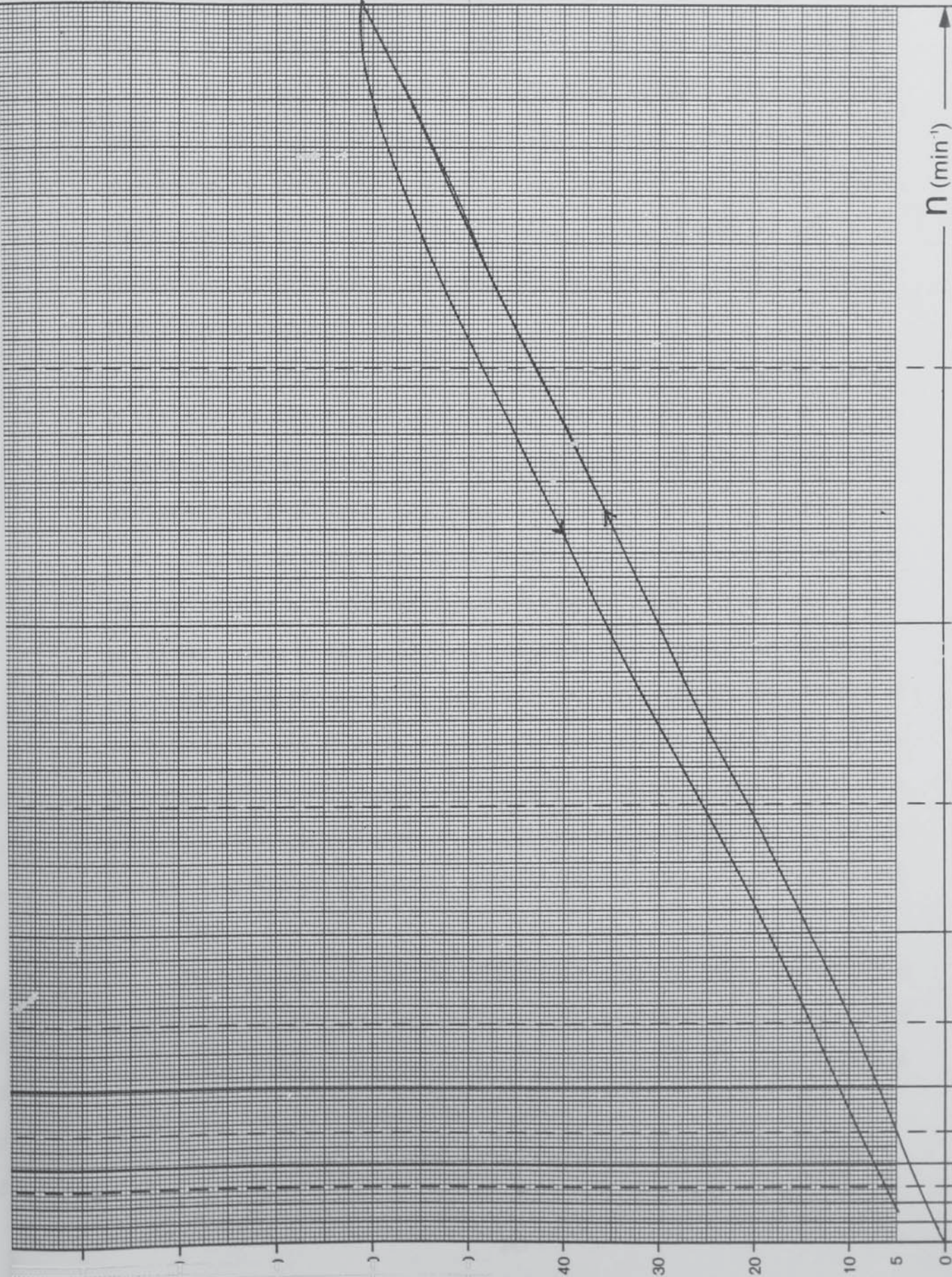


Figure 57

Sample contains
 50% Volcanic Phlegm
 in a 50% water

problems. However, more effective distribution does reduce viscosity; and certainly makes mixing easier when shear is applied for longer times. Removal of the shear allows the thixotropic nature to be asserted with a consequent increase in mastic viscosity: surface sagging or even slipping of the whole coating is then minimised.

Once a sample was considered properly mixed a small amount (0.5 ml) was applied to the viscometer plate and the cone lowered. The instrument was programmed and recording commenced; a ramp for a given rotation speed, from 0, over a given time period was recorded. The ramp produced could not be repeated immediately, upon cessation of the shear force, the system had to 'rest'; the viscosity gradually approaches its original value.

It was found that with a Cabosil content of 1% the time required for the mastic to 'rest' was 9.5 minutes, during this time hydrogen bonds broken by mixing are remade, at higher percentages longer is required, this would have to be taken into account with the final coating. This feature alone exhibits the thixotropic nature given to the system by the addition of cabosil. A short time span from mixing to achieving the high viscosity, is more desirable as the coating will remain in place once applied to a surface. There are further additives available to aid hydrogen bonds reforming.

After long periods on the plate, with the mastic having undergone alot of work, the system became granular and the results received were erratic, this state was permanent and irreversible and the system was 'overmixed'. "Under dispersion" is when the system is insufficiently mixed, this causes a decrease in viscosity, and the thixotropic agent does not have full effect. Various examples of this can be seen in Figure 5.8.

Erratic results may also be caused due to the high solids contents of the system; if the melamine phosphate aggregates accumulate on the plate this may lead to inaccuracies. Further complication can be expected due to the chemical reaction taking place if the test is continued for too long.

If a mixed sample was subjected to a constant rate of shear for a period of

Scherungsspannung $\tau = \dots$
 Shear stress
 Schergeschw. $D = \dots$
 Shear rate
 Viskosität $\eta = \dots$
 Viscosity



Datum
Date

Nr.
No.

Substanz
Substance

Temperatur
Temperature

ROTOVISCO RV

Meßkopf
Measuring head

Meßeinrichtung
Sensor system

Faktor A
Factor

Faktor M
Factor

Faktor G
Factor

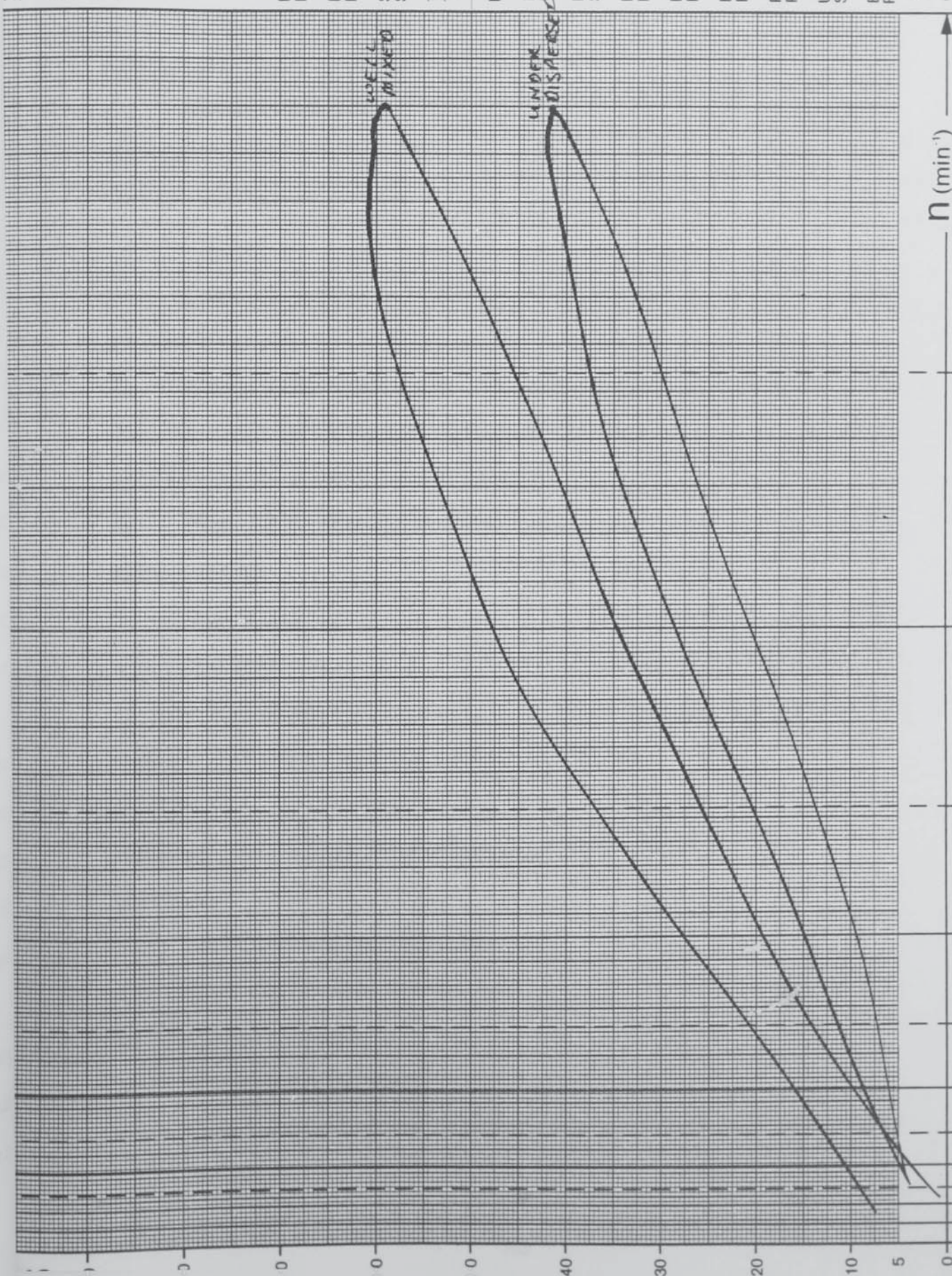
Programm
Program

Unterschrift
Signature

Bemerkungen:
Remarks:

Figure 58

Under dispersion



time, it was found that after a period of 3-4 minutes an equilibrium situation had been reached, this is shown in Figure 5.9.

Toxicology

Cabosil fumed silica is amorphous and does not possess the fibrogenic potential of many crystalline silicas, and recent tests with laboratory animals [24] have given the following results.

- i) Acute Oral Toxicity. 10 albino rats administered with an oral dose of 5 grams per kilogram of body weight all survived the 14 day duration of the study.
- ii) Primary Dermal Irritation. Where the fumed silica was applied under impervious bandages to clipped, intact and abraded skin of albino rats, the fumed silica was considered inert to mildly irritating.
- iii) Primary Eye Irritation. Here the fumed silica was considered inert to very mildly irritating.
- iv) Acute Dust Inhalation. A group of 10 test rats were exposed to an atmosphere with a gravimetric concentration of 2.08 mg/l of fumed silica for a 4-hour period for 14 days. No animals perished during the exposure, or in the 14 day period after exposure. At necropsy, no gross lesions were observed.

Handling and Storage Recommendation [24]

Handling

- i Avoid continued excessive inhalation
- ii Work area should be well ventilated
- iii Use eye protection
- iv Use protective oils/gloves
- v Fumed silica spillage can be handled using broom, vacuum, or wet absorbent material

Shear stress $\tau = A$
 Schergeschw. $D = M$
 Shear rate
 Viskosität $\eta = G$
 Viscosity



Datum
Date

Nr.
No.

Substanz
Substance

Temperatur
Temperature

ROTOVISCO RV

Meßkopf
Measuring head

Meßeinrichtung
Sensor system

Faktor A
Factor

Faktor M
Factor

Faktor G
Factor

Programm
Program

Unterschrift
Signature

Bemerkungen:
Remarks:

STATE FOR WELL
WORKED SAMPLE.

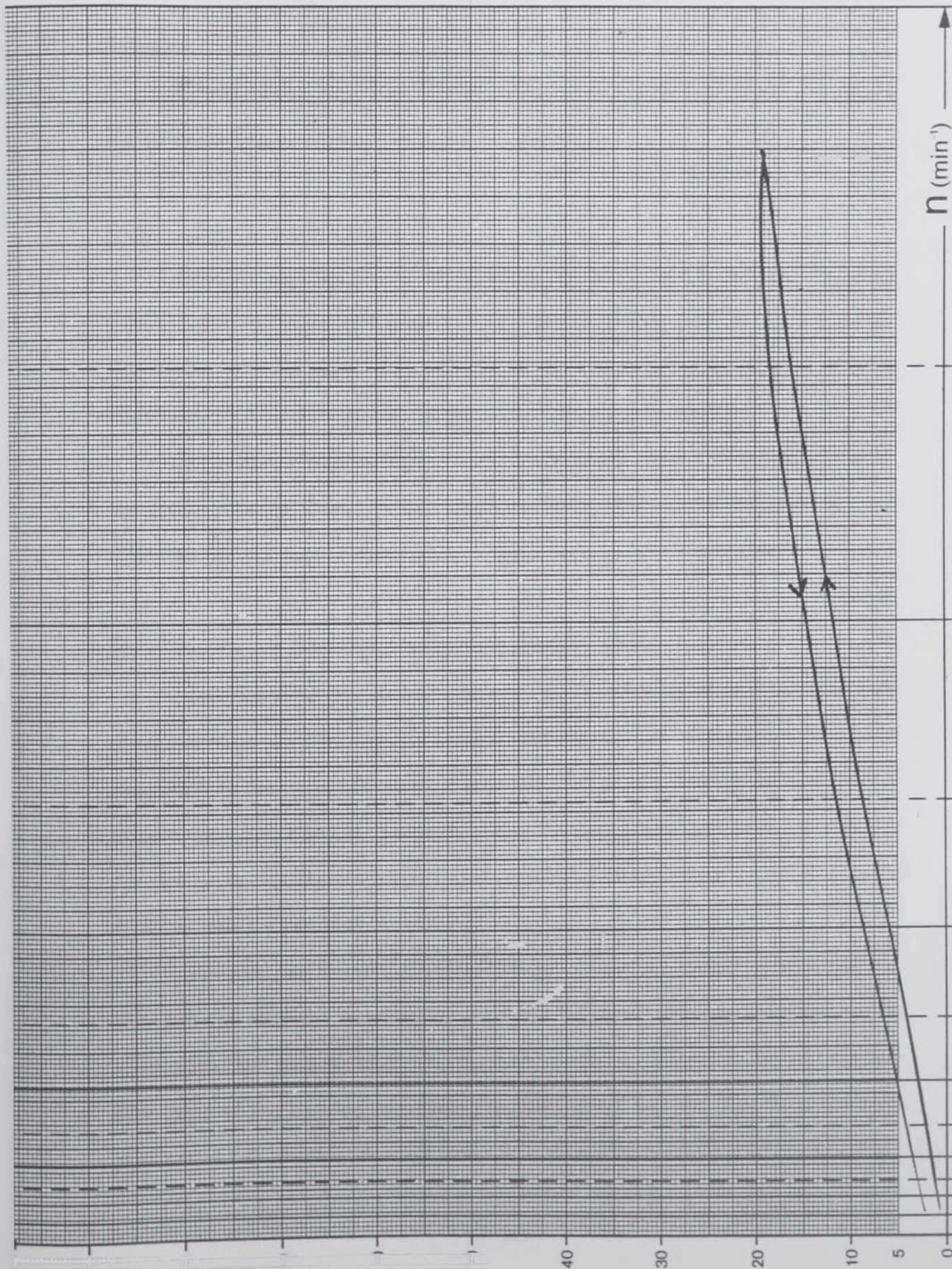


Figure 9

- vi As with many dry powders, fumed silica is subject to a build-up of static electrical charges.

Storage

Cabosil fumed silica should be stored in a dry environment, away from chemical vapours, to maintain its purity and properties.

Other uses of fumed silica

Fumed silica has many areas of use, some of the more common being reinforcement, glass reduction, anti-slip, anti-blocking, insulation, free flow and anti-caking of solids, etc. Its use as a thickener or thixotropic agent covers many areas of work including explosives, greases, paints, polyesters and printing inks.

It has uses in animal feeds, cosmetics, fertilisers, foods, insecticides, pharmaceuticals, polishes, waxes, rubbers and many more areas. These are shown in Table 5.2 where the different characteristics exhibited by each product are given.

Fire Testing of Samples Containing Fumed Silica

Samples containing different percentages of fumed silica were fire tested and compared with samples containing no fumed silica. The amount of fumed silica contained in the samples varied from 1% to 5% and in each case a marked improvement was noted in char performance. It could be seen during the fire test that the char produced was less friable and though it did not intumesce to the same extent, it did insulate the substrate.

After the fire test was complete and the sample had cooled, closer inspection revealed that the char structure had changed, the previously irregular honeycombe composition had been replaced by a network of small equally sized pores, with very few large voids, this led to a stronger more durable char. The silica particles themselves will add extra strength to the char. The different samples are compared in

Table 5.3
Cab-O-Sil's functions in coatings

Coating ¹	Anti-caking	Anti-sag	Edge Coverage	Emulsification	Fluidization	Free Flow	Gloss Reduction	Hold-out	Suspension ²	Thickening ³	Thixotropy ⁴
Epoxies		●					●		●	●	●
Lacquers		●					●		●	●	●
Paints		●	●	●			●	●	●	●	●
Polyamides		●	●							●	●
Varnishes		●					●			●	●

¹ Coatings are liquid except where otherwise noted.

² Suspension of pigments or undissolved resins.

³ Sometimes called Bodying.

⁴ Sometimes called Puffing.

Table 5.3 (a)
Cab-O-Sil's Functions in Coatings

Coatings	Anti-caking	Anti-sag	Edge coverage	Emulsification	Fluidization	Free flow	Gloss Reduction	Hold out	Suspension	Thickening	Thixotropy
Epoxies		✓					✓		✓	✓	✓
Lacquers		✓					✓		✓	✓	✓
Paints		✓	✓	✓			✓	✓	✓	✓	✓
Polyamides		✓	✓							✓	✓
Varnishes		✓					✓		✓	✓	✓

FIGURE 5.10

Fire test of samples containing 1%, 3%, 5% cabosil M-5 30% small needles of melamine phosphate $(C_3H_6N_6)_{1.2}H_3PO_4$

Distance from burner 22cm

- Sample containing 1% cabosil
- △ Sample containing 3% cabosil
- * Sample containing 5% cabosil
- Sample containing 0% cabosil

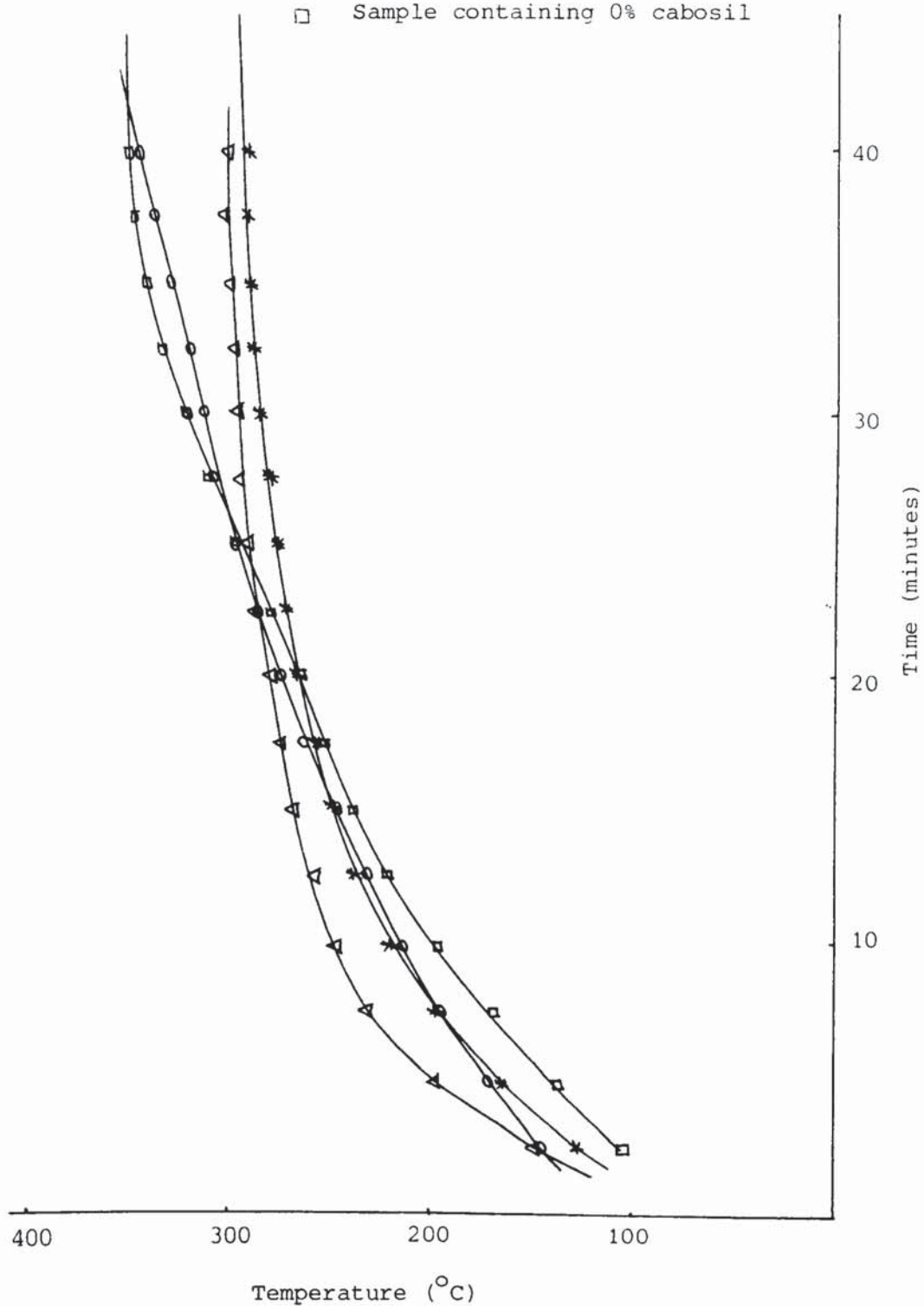


Fig 5.10. It can be seen that the larger percentages give a better insulating char, but the improvement produced must be weighted against the cost of addition; a thicker coating may reduce the amount of fumed silica required for the same insulating effect.

5.3 SOLVENTS

Solvents offer an alternative method of reducing the viscosity for the mixing process. They act as a diluent, and then evaporate to leave the original starting materials. The properties such a solvent must have therefore are,

- a) they must be compatible with the system
- b) they must not adversely affect the system
- c) they must evaporate off easily, ie high evaporation rates, high volatility,
- d) they must not be toxic.

It must also be noted that alcohols reduce the pot life of Araldite/Versamid and this should be taken into account if purchased already diluted. Various compounds have been suggested in the literature these being methyl isobutyl ketone and toluene [16], xylene [29], toluene [29], isopropanol [29], cydohexanol [29], trimethyl benzene [25]. The toxicity ratings were obtained for the more common solvents as follows:

Solvent	Maximum concentration for exposure by inhalation, ingestion and skin absorption (ppm/air)
Butanol	100
Xylene	100
Isopropanol	100
Toluene	0.02
Cydohexanol	50

It has also been suggested that isopropanol is a suitable solvent to be used in paint

spraying [12].

Using isopropanol as a solvent the mastic was tested firstly using the Haake viscometer, and then fire testing the samples produced.

Various samples were tested for viscosity at constant shear rate, with percentages varying from 1% up to 10%. It was shown that a sample containing 10% isopropanol at time = 0 minutes, gave the same trace after 5 minutes as a sample containing 4% at time = 0 minutes. This is shown in Figure 5.11.

The samples produced were examined before fire testing, noticeable characteristics were (a) the lack of surface air bubbles and (b) the gloss surface finish, both due to the reduced viscosity on application.

On fire testing the samples, the only difference noted was an initial excessive flaming, which lasted for about 3½ minutes. This flaming was not increased by increasing the percentages of solvent used. This can be seen in Figure 5.12. The final char produced was visually similar to that produced by samples containing no solvent.

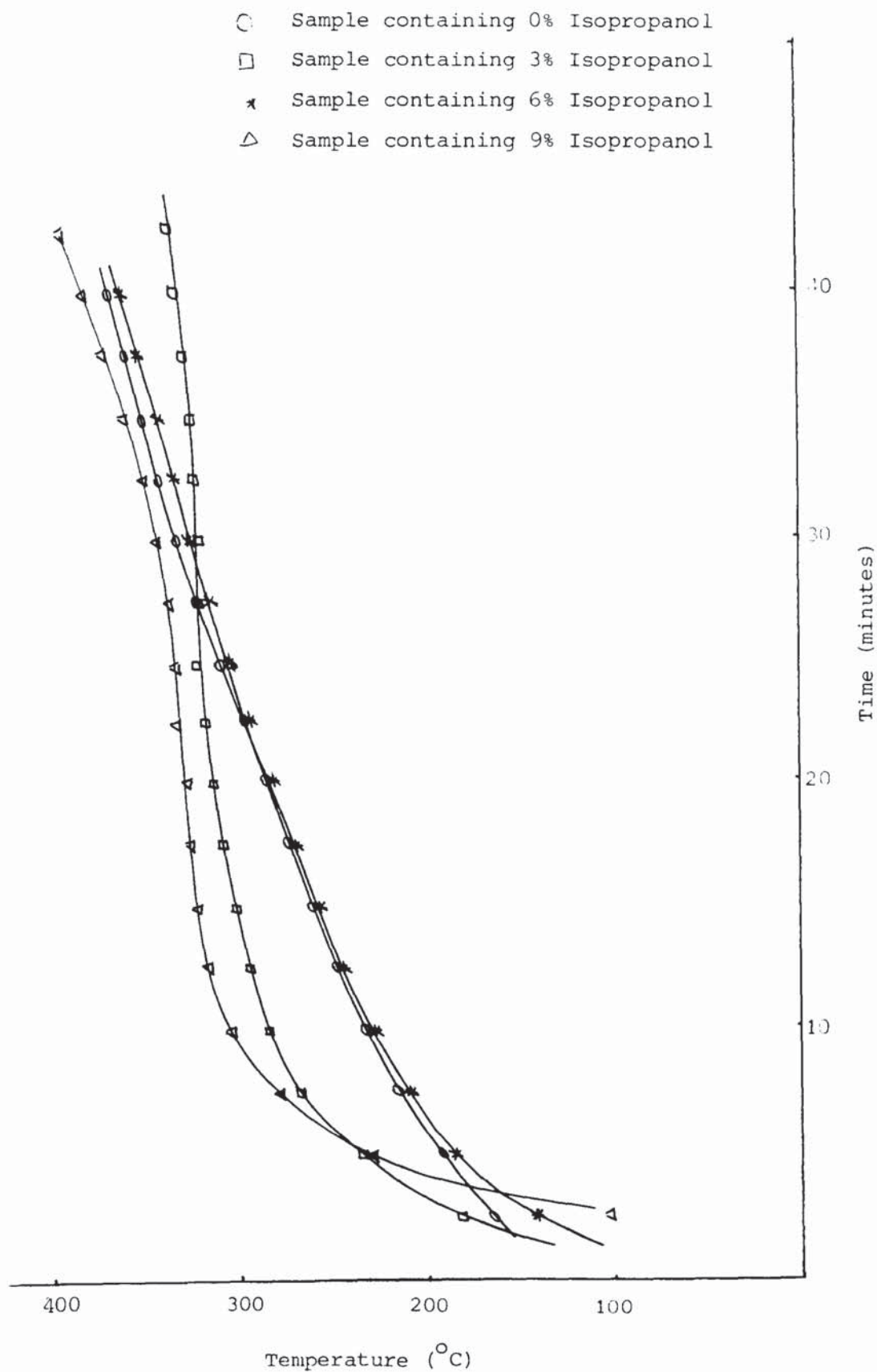
5.4 EXPANDING GRAPHITE

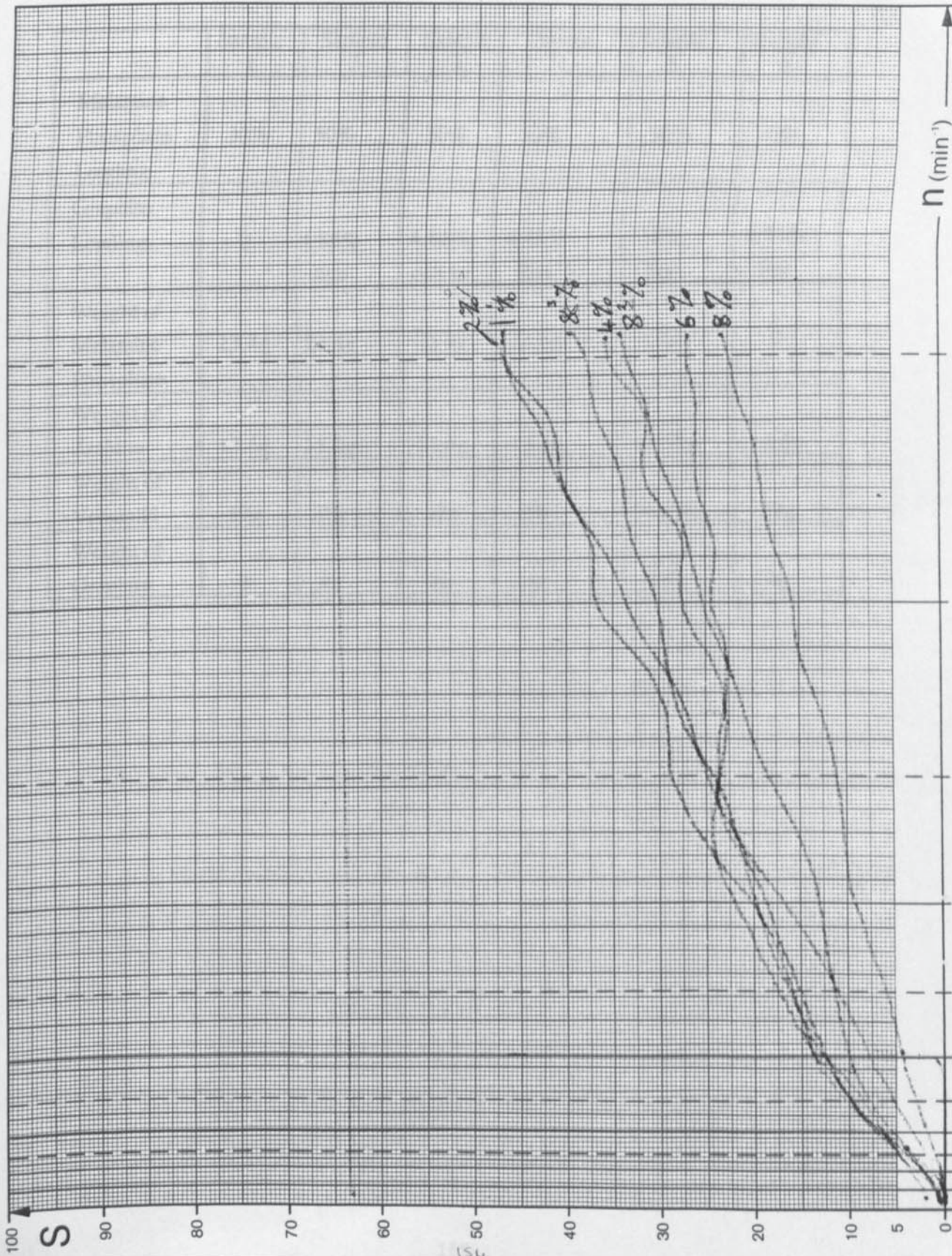
There are various forms of 'expanding graphite', all being derived from a naturally occurring mineral ore. They are forms of an intercalated graphite compound, that is designed to give a high volumetric expansion on exposure to high temperatures. Two such compounds are ex-graphite GF/99 and 2C/90, both are produced for Foseco Technik Limited in South Africa, the latter being a high purity compound with a carbon content of 99% (excluding exfoliants).

A 1980 Japanese patent [28] mentions the use of expansive graphite and phosphorus in fire protective compounds, with the graphite to phosphorus ratio being 100:(S-300). The aim of the investigation using the two graphite types was to determine the extent of any effects on the coatings characteristics. For example mixing characteristics, ease of application, extent of intumescence, insulation effects of the expanded char and durability.

FIGURE 5.12

Fire test results of samples containing 1 to 10% of isopropanol. Melamine phosphate type small needles $(C_3H_6N_6)_{1.2}H_3PO_4$
Distance from burner 22cm





Schubspannung $\tau = A \cdot S$ (Pa)
Shear stress

Schergeschw. $D = M \cdot n$ (s⁻¹)
Shear rate

Viskosität $\eta = \frac{G \cdot S}{n}$ (mPa · s)
Viscosity



Datum
Date

Nr.
No.

Substanz
Substance
STANDARD
SAMPLE

Temperatur
Temperature

ROTOVISCO RV

Meßkopf
Measuring head
CONE/PLATE

Meßeinrichtung
Sensor system

Faktor A
Factor

Faktor M
Factor

Faktor G
Factor

Programm
Program
1 MIN RAMP
→ 9 R.P.M

Unterschrift
Signature

Bemerkungen:
Remarks: PERCENTAGE

ADDITION OF ISOPROPAN

8² :- 8% AFTER 5 MINS

8³ :- 8% AFTER 10 MIN

Figure 5.11

TABLE 5.4

SAMPLES CONTAINING MELAMINE PHOSPHATE, ARALDITE, VERSAMID
AND GRAPHITE

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Melamine Phosphate Loading	30%	30%	30%	30%	30%	0%
Graphite Loading	0	4.86% fine	4.86% coarse	4.86% fine	10% fine	4.86% fine
Weight of Melamine Phosphate	23.4g	23.4g	23.4g	23.4g	17g	0
Weight of Araldite	15.6g	15.6g	15.6g	15.6g	11.53g	15.6g
Weight of Versamid	39g	39g	39g	39g	28.83g	39g
Weight of Graphite	0	4g	4g	4g	6.4g	4g

The tests were carried out using a 30% loading of melamine phosphate and a 4.86% to 10% loading of graphite (shown in Table 5.4 and Figures 5.13 and 5.14). It was found that as the solids content increased so did the viscosity, and with a graphite content of 10% the lubricating effect of the graphite made mixing extremely difficult, as was the application of the coating to the plate.

During the fire test, the first noticeable difference was the complete lack of flaming, which normally accompanies the fire testing of samples containing only the mastic and melamine phosphate. The next noticeable difference was the initial growth of small 'whiskers' from the surface, this was before the intumescence commenced. When intumescence did start no bubbling could be seen on the surface and when the sample had cooled it was found that small even sized voids had been produced, not the irregular honeycomb structure found in the char when only melamine phosphate and mastic were in the sample. The latter situation produces a better insulating and stronger, more durable char; this sample did not appear to deteriorate after 2 1/2 hours, whereas the sample containing only melamine phosphate was found to breakdown after only 50 minutes. The sample containing graphite was found to shrink on cooling, leaving cracks in the sample, normally around the edges.

When examining the temperature profiles, it can be seen in the case of samples containing graphite initially there is a sharp rise in temperature, apparently due to the increased heat conductivity of the graphite, this then plateaus and finally rises gently, due to heat conduction across the voids. It was noted at the lower percentages of graphite (4.86%) intumescence was suppressed, though at the higher percentages (ie 10%) it was increased. In one extreme case a sample containing 16% graphite intumesced to such an extent that it could not support its own weight and broke off, this would indicate that the upper limit of graphite contained in the formulation would be governed both by the physical strength of the char and by the cost.

It should also be noted that higher percentages of graphite in a sample leads to

FIGURE 5.13

Fire test results of samples containing free graphite

melamine phosphate type small needles $(C_3H_6N_6)_{1.2} H_3PO_4$

Distance from burner 19cm

△ Sample containing no graphite

* Sample containing 4.86% of fine expanding graphite

◻ Sample containing 10% of fine expanding graphite

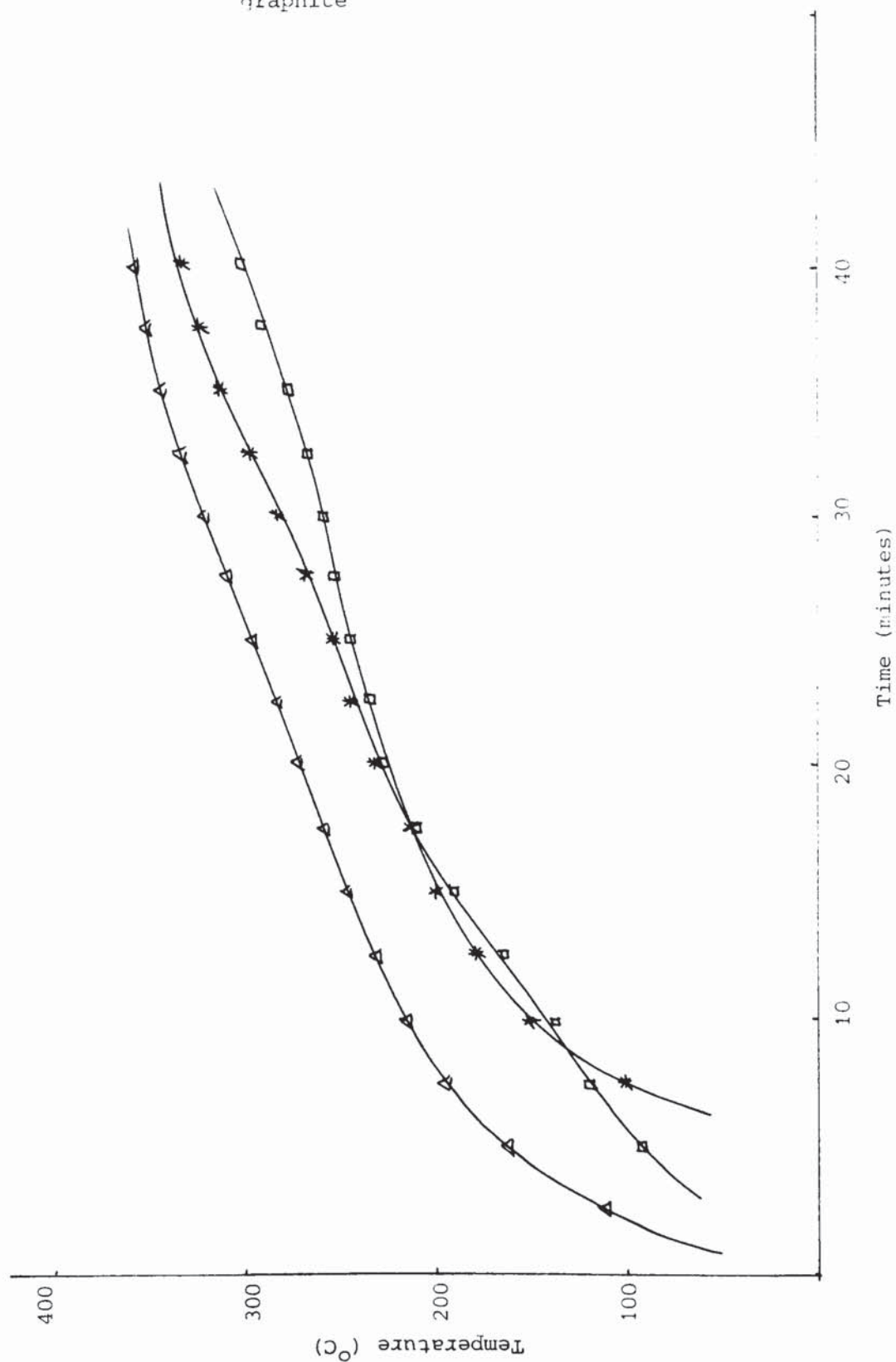


FIGURE 5.11.

Fire test results of samples containing coarse graphite. Melamine Phosphate type Small needles
 $(C_3H_6N_6) 1.2 H_3PO_4$

Distance from burner 10cm

* Sample containing 4.36% of coarse expanding graphite

□ Sample containing no graphite

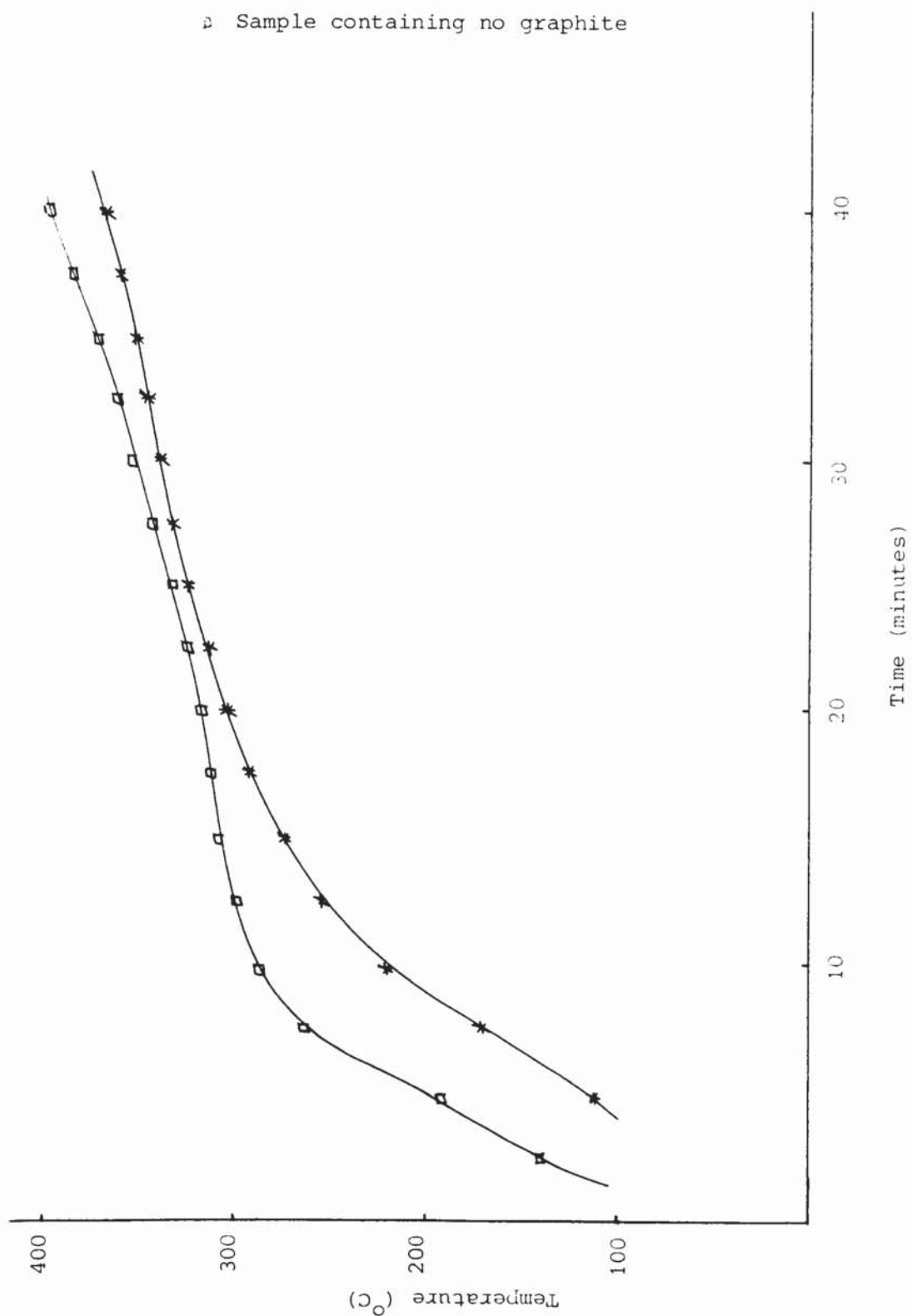
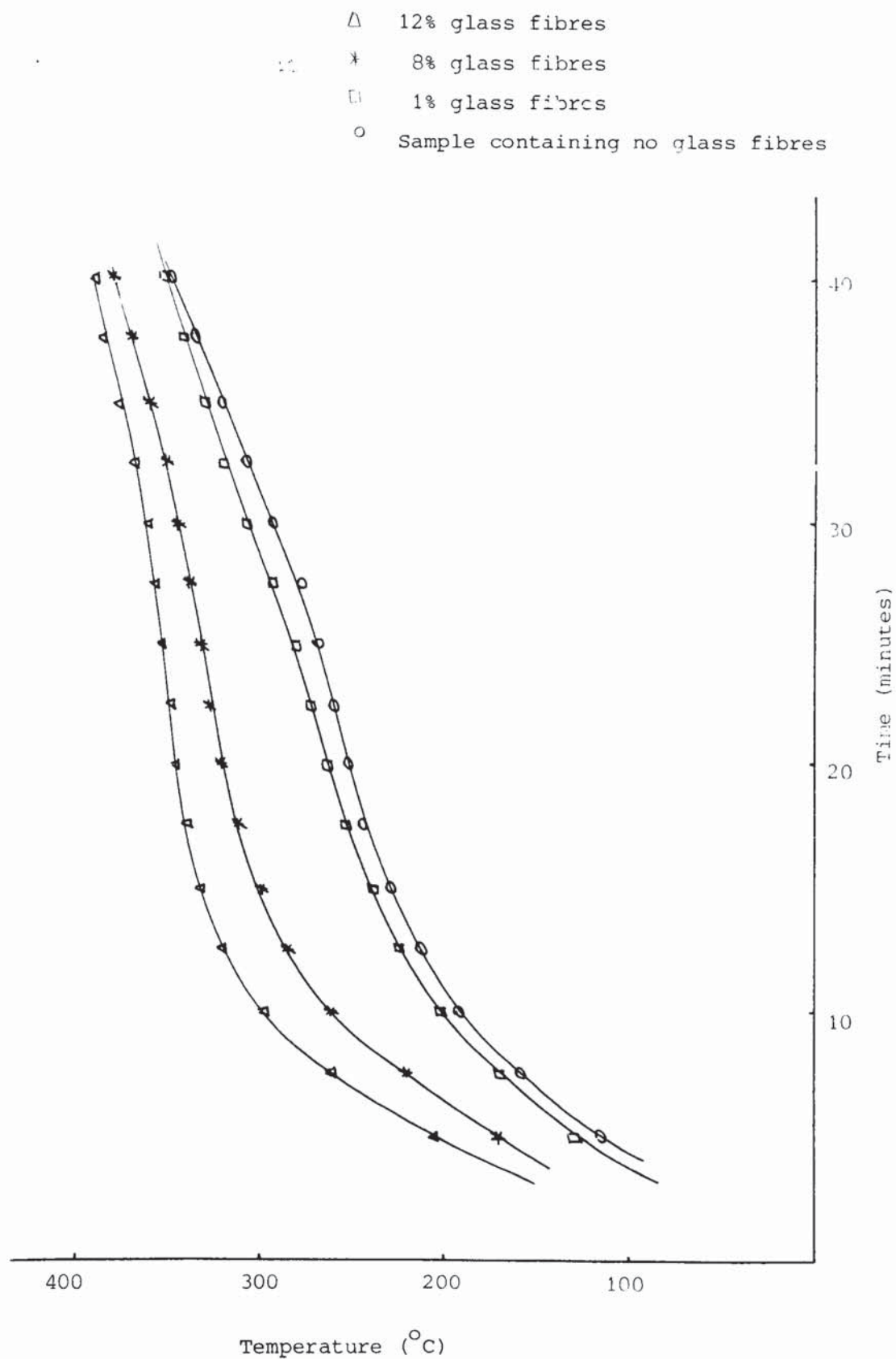


FIGURE 5.15

Fire tests of samples containing between 1% and 15% of glass fibres. Melamine phosphate type small needles $(C_3H_6N_6)_{1.2}H_3PO_4$

Distance from burner 22cm



a better insulating char.

The one main disadvantage of such a coating is its aesthetic affect, it produces a mottled grey finish which may not be pleasing to the eye.

One test not included in the above section is one incorporating graphite in the mastic, no melamine phosphate was included. On fire testing the sample exploded, this was due to the graphite expanding below the softening temperature of the mastic, the full 'cure' had not been allowed to take place in the absence of melamine phosphate.

5.5 GLASS FIBRES

The foamed char in many cases is too friable and too light to prevent breakdown during the fire, it requires a supporting structure. This may be implemented by incorporating an 'inert' substance that plays no part in the intumescent reaction, but acts as a mechanical support once foamed.

One such substance mentioned in many patents is glass fibres, which, once incorporated in the sample with the melamine phosphate will remain in place until the sample intumesces during a fire. The fibres then remain in the char and act as a support. Some glass fibres were incorporated in the mastic, though the high viscosity with the higher percentages of fibres made it increasingly difficult, and once cured the samples were fired. The sample did not intumesce as much as normal, and the insulation effects of the char were grossly reduced. However, the char did not breakdown until 2 hours after the start of the fire test.

Some samples which were not sufficiently mixed did show some signs of breakdown after 1 1/2 hours, this was shown by localised pitting.

The fire tests can be seen in Figure 5.15, with percentages varying from 1% up to 15%.

CHAPTER SIX
CONCLUSIONS

CHAPTER SIX

CONCLUSIONS

6.1 General Conclusions

Having completed the practical work and analysed the final results it would appear that most of the major problems associated with this intumescent mastic have been resolved. A suitable formulation can be mixed, applied and cured and in the event of fire will insulate the substrate against the attack of heat. The mastic system would be versatile enough to cater for special applications which could be wanted and a coating developed for each individual case. It was found that excessive heat during curing caused an 'over-cure' and the resulting coating on exposure to fire acted as a flammable tar. Normal external weathering had no detrimental effect on the coating, and in the formulation tested improved its resistance to fire. Another advantage of this type of fire protective coating is its noncorrosive nature, it does not attack or degrade the substrate to which it has been applied, and, unless cracks form, acts as a protective coating during normal times.

6.2 Standard Formulation

Various melamine phosphate types are suited to different situations, for example, for petroleum fuelled fires small/medium needles of stoichiometry $(C_3H_6N_6)_{1.0}H_3PO_4$, or medium needles of stoichiometry $(C_3H_6N_6)_{1.2}H_3PO_4$ or small block plates of the same stoichiometry are suggested. While at lower temperature fires [10] thin reflective plates treated at 210 °C or large needles of stoichiometry $(C_3H_6N_6)_{1.2}H_3PO_4$ and dried at 110 °C were found to give the best protection. As the formulation produced was to be tested in a high temperature fire the former crystal types were compared. The cheapest to produce would be the medium needles of stoichiometry $(C_3H_6N_6)_{1.2}H_3PO_4$, since the reaction is at room temperature with equal quantities with melamine and phosphate. Comparison of its intumescent performance of the more expensive $(C_3H_6N_6)_{1.0}H_3PO_4$,

indicated that there appeared to be very little advantage in using the latter option.

As the weathering tests showed that heat treatment was not necessary, and in this crystal type it caused a detrimental effect so it was not implemented. 'Heat curing' was not found necessary, the coating was allowed to 'cold cure' for at least 7 days at temperatures in excess of 15 °C, or for 20 days at temperatures in excess of 5 °C.

The melamine phosphate was included in the mastic, Araldite and Versamid in the ratio 5:2.

6.3 Problems with Large Scale Production

The major problems with the large/commercial scale production of melamine phosphate was the solid separation/.drying stage, as the melamine phosphate is of small particle size, has a tendency to form agglomerations, and is affected by high drying temperatures, many drying methods had to be discounted. Two suitable drying systems identified were Indirect dryers and Vacuum Rotary dryers, neither have large volumes of air passing through the drying vessel or use excessive drying temperatures.

A batch reactor was used for the production route and the dried product stored in sealed containers as the solid is hygroscopic.

6.4 Mastic preparation and application

The coating was prepared by mixing the melamine phosphate with the Araldite and then adding the Versamid, the viscous mixture was then applied to a clean unprimed surface, where larger surfaces were involved priming is recommended.

6.5 Fire Testing

It was found that the fire test rig gave repeatable results, normally 2 or 3 samples prepared in exactly the same way, were tested and the results compared, this ensured that errors were eliminated. Use of the video monitor and computer facilities also enable the tests to be re-examined at leisure after the experiment was completed and compared

directly with other results.

6.6 Modified Formulations

The necessity for a thixotropic additive was found on mixing and applying the mastic, ie a reduction in viscosity for mixing, and an increase in viscosity once applied. the additives used were Cabosil M-5 and H-5, both are fumed silica. Due to their nature they were difficult to disperse, but once completely mixed produced a reduction in viscosity, and so allowing the coating to be sprayed. Once applied the sample had a greater tendency to remain on a flat vertical surface. Varying amounts were incorporated, from 1%-5%, it was found that at the higher percentages it was extremely difficult to mix the system, while at the lower percentages, very little thixotropic affect was imparted to the system. 3%-4% was found to increase the final viscosity sufficiently, while still allowing mixing of the system. The addition of iso-propanol reduced the viscosity of the system still further to allow mixing and then quickly evaporated to leave the original system. Use of solvents made the mixing of the mastic easier and did not affect the coating on application, nor did it affect the fire testing of the cured sample.

Both glass fibres and expanding graphite were included in the coating and both reduced intumescence but produced a longer lasting char. The glass fibres had no additional benefits, they increased heat conduction across the char so producing a less insulating char. The expanding graphite produced a more regular honeycomb structure in the char which had small voids, thus produced a better insulating char, which did not breakdown after extended fire tests.

A thixotropic agent, a solvent and expanding graphite could all be included in the formulation, allowing easier mixing and application, thus producing a more durable and insulating char.

CHAPTER SEVEN
RECOMMENDATIONS FOR FURTHER WORK

CHAPTER SEVEN

RECOMMENDATIONS FOR FURTHER WORK

In all major areas of interest in this research large scale production of melamine phosphate, mastic preparation and application and fire testing, there exists scope for further work. Recommendations are given for each of these areas.

7.1 Large Scale Production of Melamine Phosphate

It was found that the major problems with large/commercial scale production of melamine phosphate was the solid separation/drying stage, due to the small particle size of melamine phosphate, and although two suitable drying systems were identified, neither were used. Future research in this area should involve investigation into both of these dryers, Indirect dryers and Vacuum Rotary dryers. Different drying time/temperature cycles could be investigated, with a view to minimising costs.

7.2 Mastic Preparation and Application

With the reduced viscosity brought about by the addition of thixotropic agents and solvents, the system is easier to mix, the spraying of such a coating would require further examination, and a suitable application method devised. The method may depend on the solids content and extent of the thixotropic effect.

7.3 Multiple Coats

If the cured mastic is prone to attack from the atmosphere a sealing protective coat could be devised that would protect the outer coat and not have an adverse affect on the intumescent properties of the coating. This is also a way to improve the aesthetic appearance of the mastic.

If a single coating of suitable thickness cannot be applied to a vertical surface, multiple thin coatings may provide the solution.

7.4 Modified Formulations

Having found the advantageous effects of thixotropic additives, solvents and graphite, a single system containing all three to produce a system that has a reduced viscosity for preparation, that increases for application and still has the final char stability and insulating affects would be desirable.

Further work would be required into various combinations of solvents, to produce a quickly evaporating solvent that is non-toxic and does not affect the intumescent qualities of the mastic.

7.5 Specific coatings

Once the above problems have been solved special coatings could be devised, with different time/temperature test responses suitable for different situations.

The recommended formulation for future work, in a high temperature fire situation would be

- a) A mastic containing 30% Melamine Phosphate in a ratio of 5:2, Araldite:Versamid.
- b) 4% Cabosil
- c) 5% Expanding Graphite
- d) 2% Isopropanol.

APPENDICES

APPENDIX 1

EVALUATION OF VISCOSITY USING HAAKE ROTOVISCO VISCOMETER

APPENDIX I

Evaluation of Viscosity using Haake Rotovisco Viscometer

A Hoake Rotovisco RV100 is used to measure the dynamic viscosity of the intumescent paste. A PK type cone and plate sensor was used in all instances. The procedure for calibration and use is as follows:-

- i) Depress Mairs, Int and stop buttons on base unit.
- ii) Set input on plotter to $y = 50 \text{ mV/cm}$, $x = 50 \text{ mV/cm}$.
- iii) Zero 'x-axis' by setting 'E' to 1 on the digital counter and altering zero knob to obtain desired position on paper.
- iv) Turn 'E' to 'Max' and alter vernier knob to obtain required full scale deflection.
- v) Set 'E' to required sensitivity.
- vi) To calibrate 'X-axis' for rotor speed depress 'stop' button and turn 'zero' knob to set pen to desired paper.
- vii) Release 'stop' button and set maximum rotor speed then use vernier to set pen to end of scale required. Press 'stop' to fix 'x-axis'.
- viii) Release stop button to commence programme.

A plot of Torque(s) as a function of rotor speed is thus produced and it is a straight forward procedure to calculate actual viscosity:-

$$\text{Viscosity} = \frac{G \times S}{n}$$

G : Factor for any given sensor system

S : Torque reading

n : Rotational speed

For a PK sensor system as used G is 3900

The value of viscosity is given in m Pa S (1m.Pa.S = 1 centipoise).

APPENDIX 2

COMPUTER PROGRAMMES AND EXAMPLES OF COMPUTER OUTPUT

PLOTTA!

```

L. 0, 450
10 *TV255,1
20 MODE 0
30 VDU19,1,3,0,0,0
40 DIM C$(4)
50 ENVELOPE 1,1,0,0,0,0,0,0,125,-10,0,-1,125,100
60 ON ERROR GOTO 1340
70 PROCINPARAMETERS
80 @%=&20209
90 PROCAXIS
100 VDU23,60,4.79,0
110 VDU33,1,0;0;0;0;0;
120 PrevX=0:PrevY1=0:PrevY2=0:PrevY3=0:PrevY4=0:X=0
130 Totaltime=0
140 TIME=0
150 REPEAT
160 PROCTIME
170 PROCVOLT
180 PROCPLOT
190 Totaltime=Totaltime+Samptime
200 UNTIL Totaltime > Xfullscale
210 REPEAT
220 IF INKEY(-1) THEN PROCDUMP
230 UNTIL FALSE
240 END
250 :
260 :
270 DEF PROCINPARAMETERS
280 CLS
290 INPUT TAB(5,3)"Y.AXIS full scale voltage (volts) " Yfu
11 scale
300 INPUT TAB(5,5)"Y.AXIS offset voltage (volts) " Yoffset
310 LET Ypixel=(Yfullscale-Yoffset)/255
320 INPUT TAB(5,7)"Y.AXIS divisional markings (volts) " Yd
ivmarks
330 LET Ydivpixel=INT(Ydivmarks/Ypixel)
340 INPUT TAB(5,9)"X.AXIS full scale (minutes) " Xfullscal
e
350 Xfullscale=Xfullscale*60 : Xpixelsec=(fullscale/6000
360 INPUT TAB(5,11)"X.AXIS divisional markings (minutes) "
Xdivmarks
370 Xdivmarks=Xdivmarks*60 : Xdivpixel=(Xdivmarks/Xpixelse
c)
380 INPUT TAB(5,13)"Sampling Time (minutes) "Samptime
390 Samptime=Samptime*60 : Samppixel=(Samptime/Xpixelsec)
400 PRINT TAB(5,15)"Input (Y)yes or (N)no for channel requ
ired"
410 FOR NX=1 TO 4
420 PRINT TAB(5,16+NX)"Channel ";NX;" ";
430 INPUT C$(NX)
440 NEXT NX
450 ENDPROC

```

PLOTTA:

(1)


```

L. 460.700
460 :
470 :
480 DEF PROCAXIS
490 CLG
500 VDU3
510 VDU29,0;0;
520 MOVE 30,30
530 PRINT "Div-Marks = ";Xdivmarks;" Secs.  ";
540 PRINT "Sampling Time = ";Samotime;" Secs.  ";
550 PRINT"Total time = ";Xfullscale/60;" Mins"
560 VDU29,0;21*4;
570 MOVE 0,0
580 INC=0
590 FOR Y=0 TO 203*4 STEP Ydivpixel*4
600 MOVE 0,Y+17
610 PRINT;INC+Yoffset
620 MOVE 30*2,Y
630 DRAW 40*2,Y
640 INC=INC+Ydivmarks
650 NEXT Y
660 VDU29,40*2;16*4;
670 MOVE 0,0
680 FOR X=0 TO 600*2 STEP Xdivpixel*2
690 MOVE X,0
700 DRAW X,20
710 NEXT X
720 VDU29,40*2;21*4;
730 MOVE 0,0
740 DRAW 0,203*4
750 MOVE 0,0
760 DRAW 600*2,0
770 VDU4
780 ENDPROC
790 :
800 :
810 DEF PROCPLT
820 Y1=((VOLT1-Yoffset)/Ypixel)*4
830 Y2=((VOLT2-Yoffset)/Ypixel)*4
840 Y3=((VOLT3-Yoffset)/Ypixel)*4
850 Y4=((VOLT4-Yoffset)/Ypixel)*4
860 IF C$(1)="N" THEN 890
870 MOVE PrevX,PrevY1
880 PLOT3,X,Y1
890 IF C$(2)="N" THEN 920
900 MOVE PrevX,PrevY2

```

PLOTTA! (continued)
 (ii)

```

L. 910,1350
910 PLOTS,X,Y2
920 IF C$(3)="N" THEN 950
930 MOVE PrevX,PrevY3
940 PLOTS,X,Y3
950 IF C$(4)="N" THEN 980
960 MOVE PrevX,PrevY4
970 PLOTS,X,Y4
980 LET PrevX=X:PrevY1=Y1:PrevY2=Y2:PrevY3=Y3:PrevY4=Y4
990 X=X+(Sampixel*2)
1000 SOUND 3,1,245,1
1010 ENDPROC
1020 :
1030 :
1040 DEF PROCVOLT
1050 VOLT1=(ADVAL(1)/16)*(1.8/4095)
1060 VOLT2=(ADVAL(2)/16)*(1.8/4095)
1070 VOLT3=(ADVAL(3)/16)*(1.8/4095)
1080 VOLT4=(ADVAL(4)/16)*(1.8/4095)
1090 ENDPROC
1100 :
1110 :
1120 DEF PROCTIME
1130 @%=820009
1140 REPEAT
1150 SEC=(TIME DIV 100)MOD 60
1160 MIN=(TIME DIV 6000)MOD 60
1170 HR=(TIME DIV 360000)MOD 24
1180 PRINT TAB(0,1)"Time ";HR;MIN;SEC
1190 IF INKEY(-1) THEN PROCDUMP
1200 UNTIL TIME/100 > Totaltime
1210 @%=10
1220 ENDPROC
1230 :
1240 :
1250 DEF PROCDUMP
1260 Time=TIME
1270 VDU19,1,7,0,0,0
1280 *GPRINT "ANALOGUE INPUT      VOLTS ",3,2,5,1,30
1290 *GDUMP 1,1,3,1,15
1300 VDU19,1,3,0,0,0
1310 TIME=Time
1320 ENDPROC
1330 :
1340 IF ERR=17 THEN 1400
1350 ON ERROR OFF

```

```

L. 1360,1600
1360 MODE 3
1370 REPORT:PRINT" AT ";ERL
1380 END
1390 :
1400 VDU26:CLS
1410 INPUT TAB(5,5)"(R)repeat (C)change (E)end " D$
1420 IF D$="R" THEN 80
1430 IF D$="C" THEN 70
1440 IF D$="E" THEN MODE3 : END
1450 PRINT TAB(5,5)"
1460 GOTO 1410

```


PLOT

```

L. 0,430
10 *TV255,1
20 MODE 0
30 DIM CO(310)
40 VDU19,128,132,0,0,0
50 VDU5
60 Y1 = OPENIN"CO1"
70 FOR IX = 1 TO 300
80 INPUTEY1,CO(IX)
90 NEXT
100 CLOSEEY1
110 PROCCAXIS
120 PROCPLOT
130 REPEAT
140 IF INKEY(-1) THEN PROCDUMP
150 UNTIL FALSE
160 VDU4
170 END
180 DEF PROCCAXIS
190 CLS
200 YPIXEL = 0.06/235
210 YDIVPIXEL = INT(0.01/YPIXEL)
220 TT = 3
230 XPIXEL = TT/300
240 XDIVPIXEL = INT(TT/(30+XPIXEL))
250 VDU29,0;21*4;
260 MOVE 0,0
270 INC = 0
280 FOR Y = 0 TO 235*4 STEP YDIVPIXEL*4
290 MOVE 0,Y+17
300 PRINT;INC
310 MOVE 30*2,Y
320 DRAW 40*2,Y
330 INC = INC + 0.01
340 NEXT Y
350 VDU29,40*2;16*4;
360 MOVE 0,0
370 FOR X=0 TO 300*4 STEP XDIVPIXEL*4
380 MOVE X,0
390 DRAW X,20
400 NEXT X
410 VDU29,40*2;21*4;
420 MOVE 0,0
430 DRAW 0,235*4
440 MOVE 0,0
450 DRAW 300*4,0

```

```

L. 460,600
460 ENDPROC
470
490 DEF PROCPLOT
500 LET PREVX = 0:PREVY1 = 0
510 FOR X = 0 TO 300*4 STEP 4
520 IX = INT((X/4)+1)
530 IF IX = 301 THEN IX = 300
540 Y1 = (CO(IX)/YPixel)*4
550 MOVE PREVX,PREVY1
560 DRAW X,Y1
570 LET PREVX = X:PREVY1 = Y1
580 NEXT X
590 ENDPROC

```

PLOT (continued)
(ii)

1000.00

900.00

800.00

700.00

600.00

500.00

400.00

300.00

200.00

100.00

0.00

R U N N O

T E M P

C

Time 0.3.29.

Div-Marks = 300.00 Secs. Sampling Time = 6.00 Secs. Total time = 30.00 Mins

1000.00

900.00

800.00

700.00

600.00

500.00

400.00

300.00

200.00

100.00

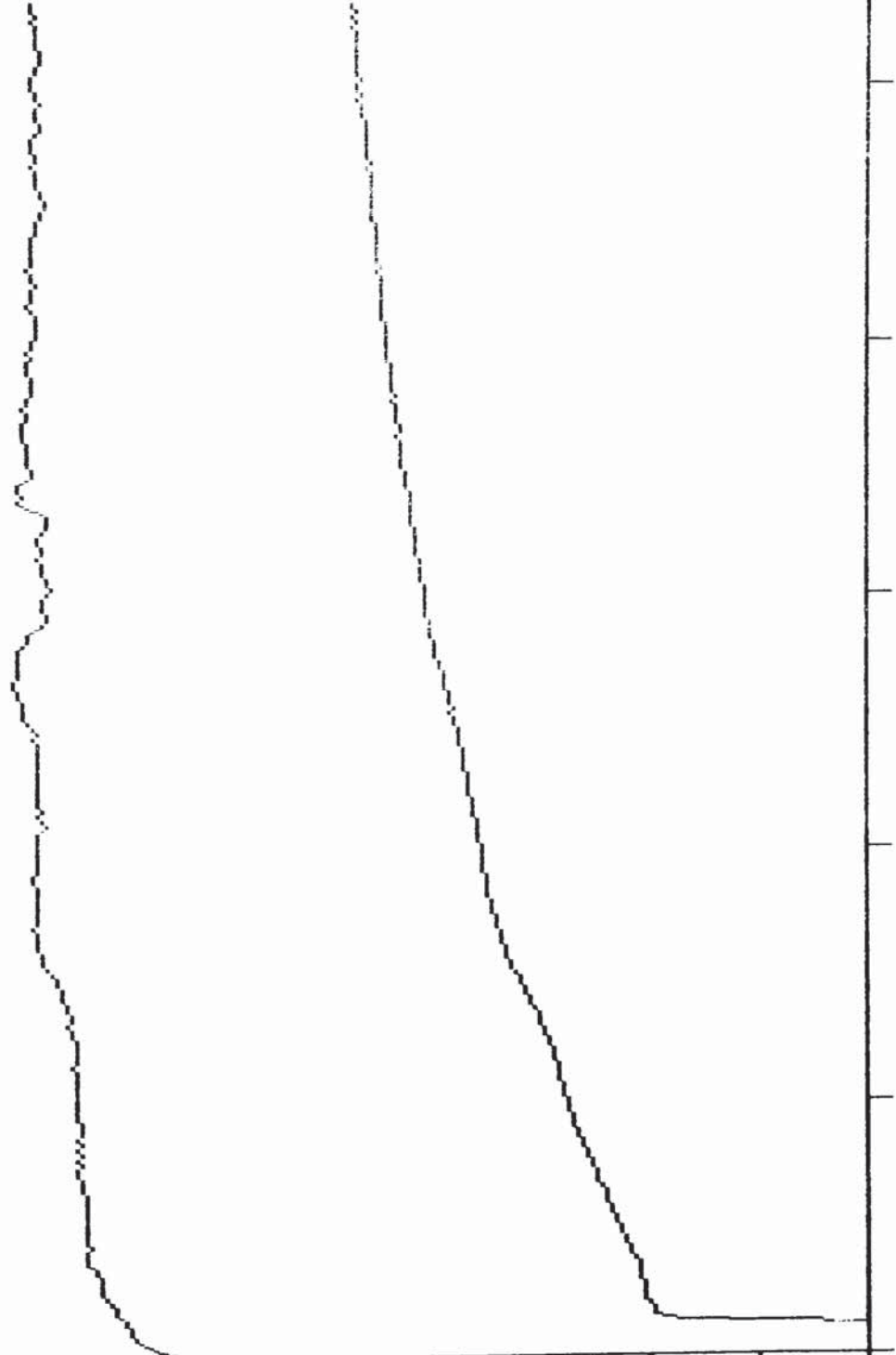
0.00

R U N N O

T E M P

C

Time 0.26.28.



Div-Marks = 300.00 Secs. Sampling Time = 6.00 Secs. Total time = 30.00 Mins

1000.00

900.00

800.00

700.00

600.00

500.00

400.00

300.00

200.00

100.00

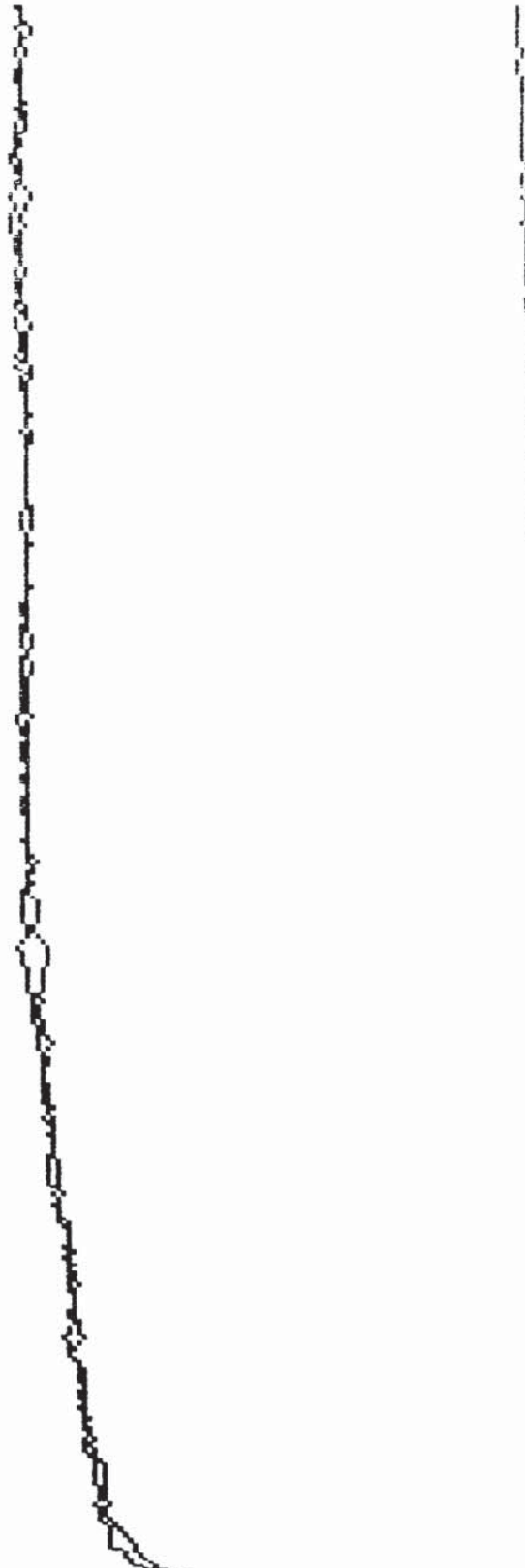
0.00

R U H M O

T E M P

C

Time 0.30.0..

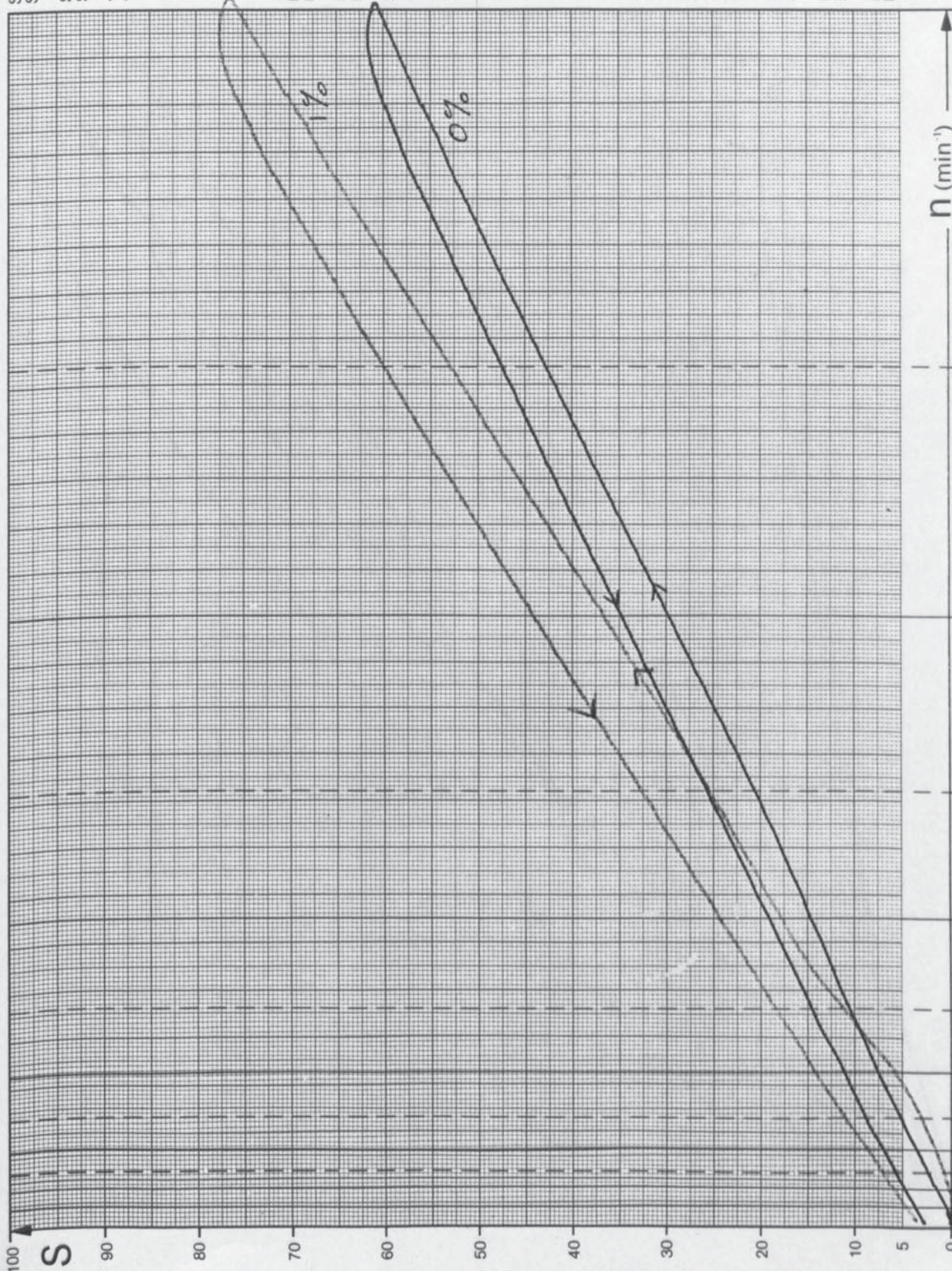


Div-Marks = 300.00 Secs. Sampling Time = 6.00 Secs. Total time = 30.00 Mins

APPENDIX 3
HAAKE VISCOMETER PLOTS SHOWN FOR VISCOSITY WORK

ROTOVISCO

Fließkurve
Flow curve



Schubspannung $\tau = A \cdot S$ (Pa)
Shear stress

Schergeschw. $D = M \cdot n$ (s⁻¹)
Shear rate

Viskosität $\eta = \frac{G \cdot S}{n}$ (mPa·s)
Viscosity



Datum
Date

Nr.
No.

Substanz
Substance

Temperatur
Temperature

ROTOVISCO RV

Meßkopf
Measuring head

Meßeinrichtung
Sensor system

Faktor A
Factor

Faktor M
Factor

Faktor G
Factor

Programm
Program

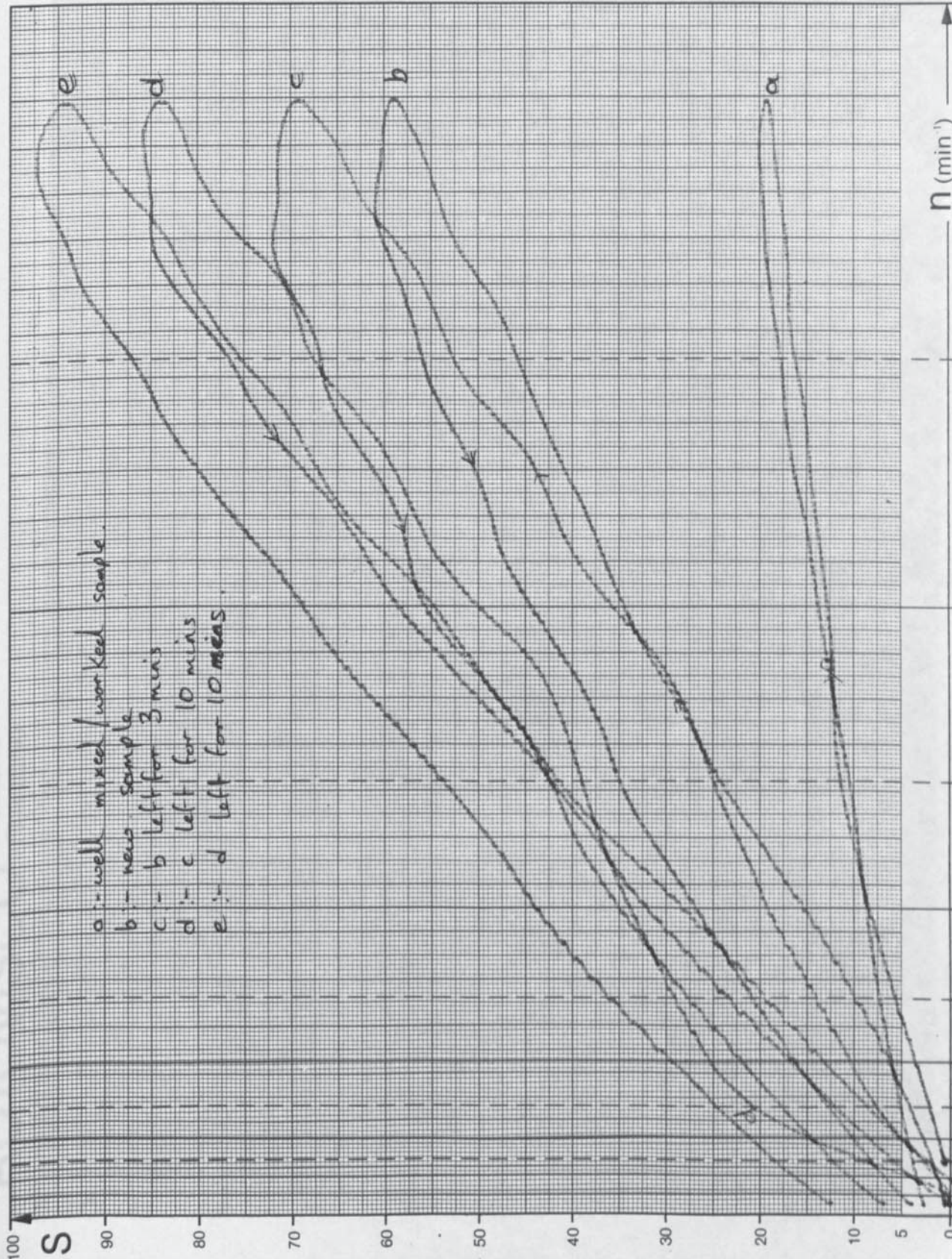
Unterschrift
Signature

Bemerkungen:
Remarks:

ADDITION OF
CABOSIL

ROTOVISCO

FlieBkurve
Flow curve



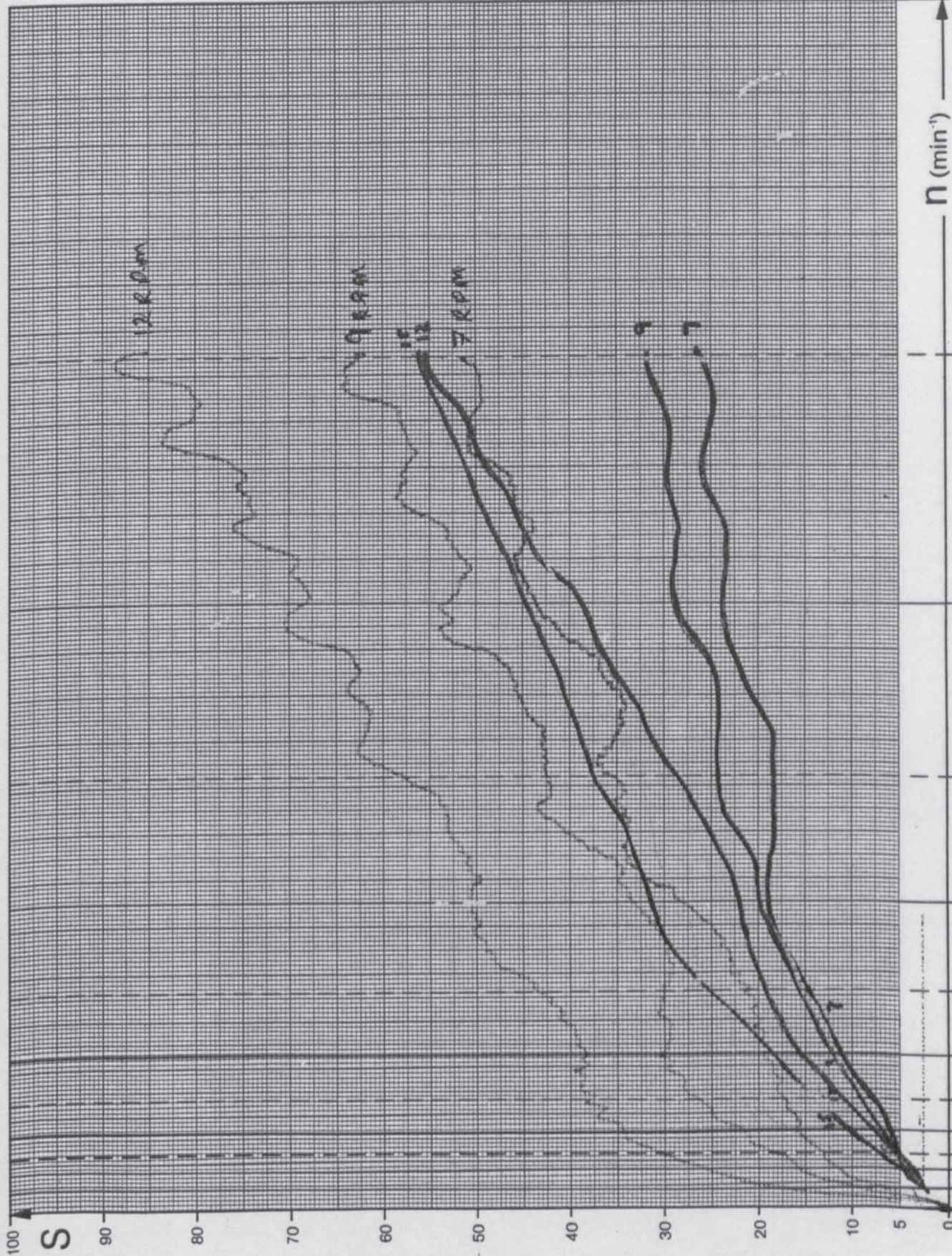
Schubspannung $\tau = A \cdot S$ (Pa)
Shear stress
Schergeschw. $D = M \cdot n$ (s⁻¹)
Shear rate
Viskosität $\eta = \frac{G \cdot S}{n}$ (mPa · s)
Viscosity



Datum
Date 17/6/86
Nr.
No.
Substanz
Substance 3% Cabosil
Temperatur
Temperature 23°
ROTOVISCO RV C
Meßkopf
Measuring head Cone + Plate.
Meßeinrichtung
Sensor system
Faktor A
Factor A
Faktor M
Factor M
Faktor G
Factor G 3900
Programm
Program 9 R.P.M
1 MIN RAMP.
Unterschrift
Signature
Bemerkungen:
Remarks: ILLUSTRATION OF
VISCOSITY CONTROL
USING 3% CABOSIL

ROTOVISCO

Fließkurve
Flow curve



Schubspannung $\tau = A \cdot S$ (Pa)
Shear stress
Schergeschw. $D = M \cdot n$ (s⁻¹)
Shear rate
Viskosität $\eta = \frac{G \cdot S}{n}$ (mPa)
Viscosity



Datum
Date

6/6/81

Nr.
No.

2

Substanz
Substance

3% Cobas

Temperatur
Temperature

23°

ROTOVISCO RV

Meßkopf
Measuring head

Cone plate

Meßeinrichtung
Sensor system

Faktor A
Factor

Faktor M
Factor

Faktor G
Factor

Programm
Program

7, 9, 12 RPM

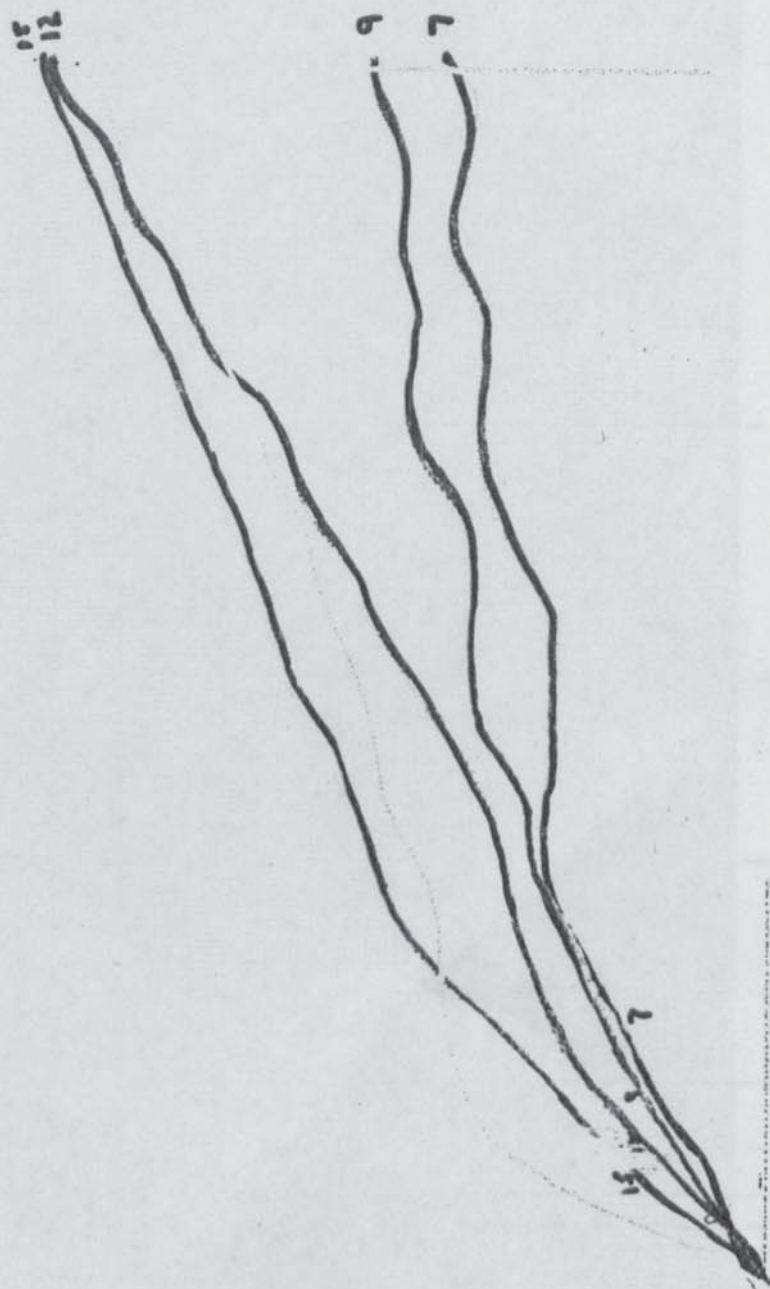
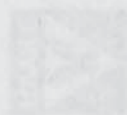
Unterschrift
Signature

Bemerkungen:

Remarks: ACETATE SHOW
CHANGE IN VISCOSITY
WHEN SAMPLE IS
CONSTANTLY WORKED
FOR 4 MINUTES

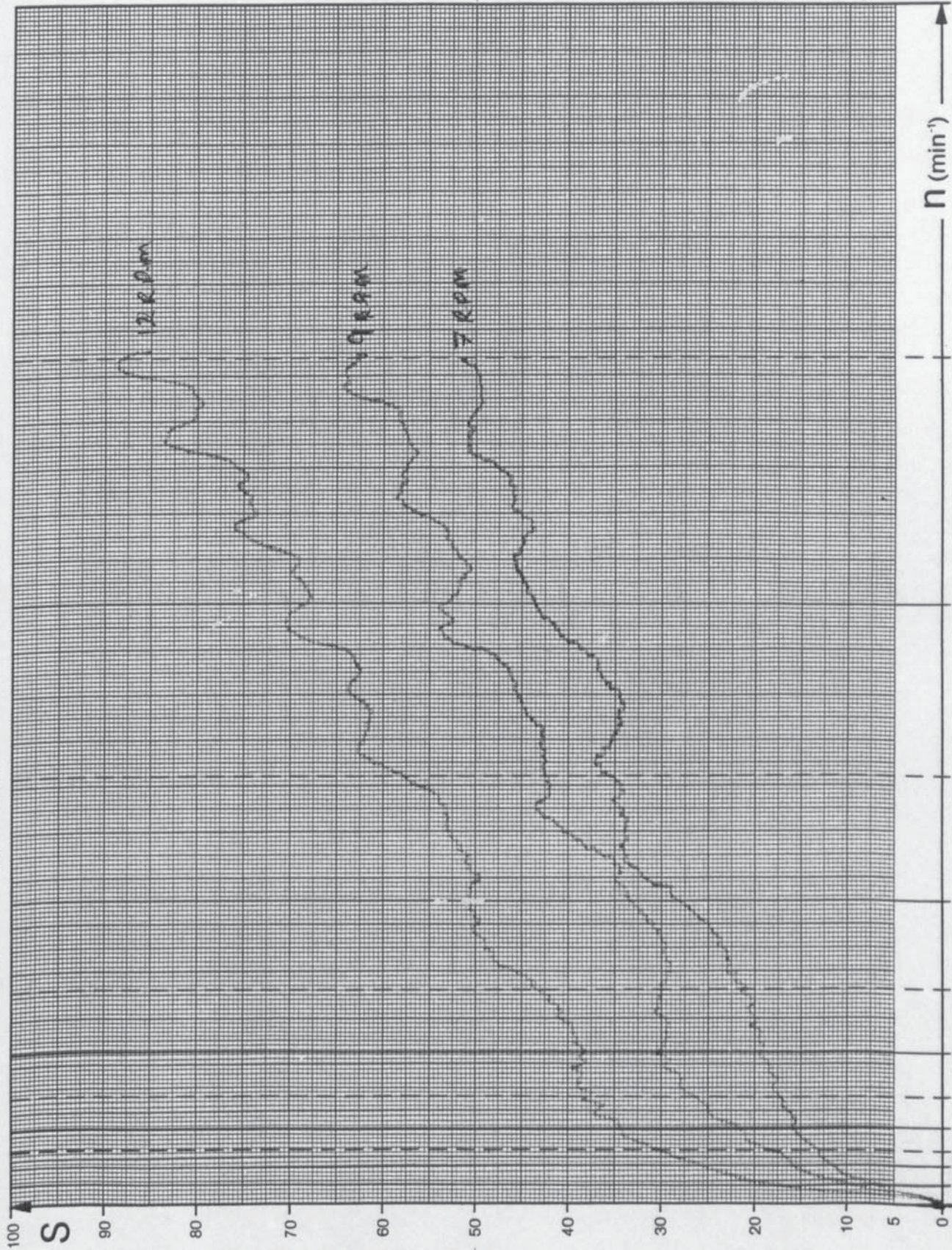
HOTOVISCO Plastivisk Flow curve

Schneiderring 1-A-2.00
Größe 1/2
Schneidring 0-14-100
Größe 1/2
Vollschüssel 1-0-3-100
Größe 1/2



ROTOVISCO

Fließkurve
Flow curve



Schubspannung $\tau = A \cdot S$ (Pa)
Shear stress
Schergeschw. $D = M \cdot n$ (s⁻¹)
Shear rate
Viskosität $\eta = \frac{G \cdot S}{n}$ (mPa)
Viscosity



Datum
Date 6/6/84

Nr.
No. 2

Substanz
Substance 3% Cobas

Temperatur
Temperature 23°

ROTOVISCO RV

Meßkopf
Measuring head Cone plate

Meßeinrichtung
Sensor system

Faktor A

Faktor M

Faktor G

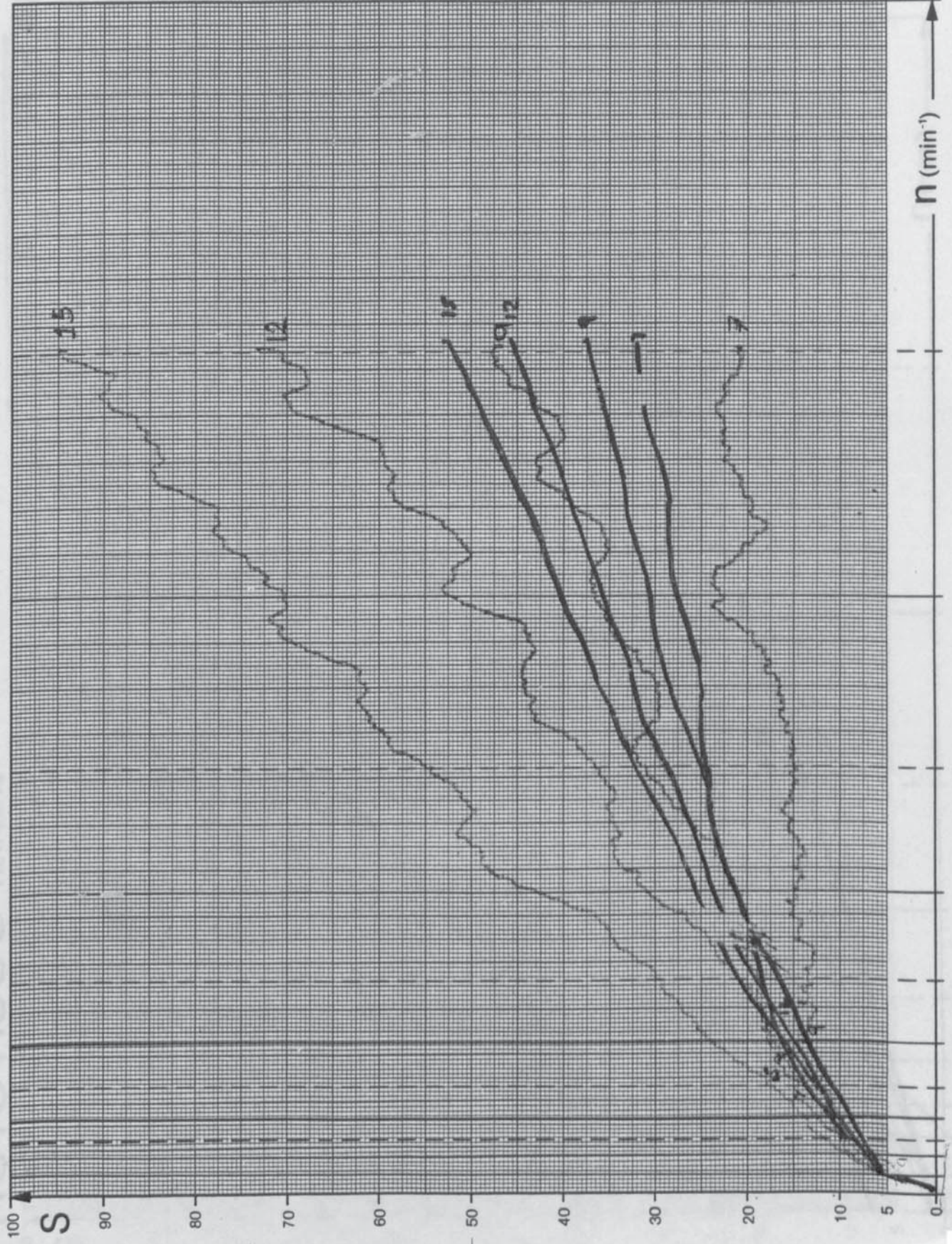
Programm
Program 7, 9, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100

Unterschrift
Signature

Bemerkungen:
Remarks: ACETATE SHOW
CHANGE IN VISCOSIT
WHEN SAMPLE IS
CONSTANTLY WORK
FOR 4 MINUTES

ROTOVISCO

Fließkurve
Flow curve



Schubspannung $\tau = A \cdot S$ (Pa)
Shear stress

Schergeschw. $D = M \cdot n$ (s⁻¹)
Shear rate

Viskosität $\eta = \frac{G \cdot S}{n}$ (mPa)
Viscosity



Datum
Date

6/6/86

Nr.
No.

3

Substanz
Substance

19a Cabosil

Temperatur
Temperature

23°

ROTOVISCO RV

Meßkopf
Measuring head

Coned plate

Meßeinrichtung
Sensor system

Faktor A

Faktor M

Faktor G

Programm
Program

Unterschrift
Signature

Bemerkungen:
Remarks:

EFFECT OF 1%
CABOSIL ON STANDARD
SAMPLE AT DIFFERENT
ROTATIONAL SPEEDS

ROTOVISCO

ROTATIONAL VISCOMETER

Flow Curve

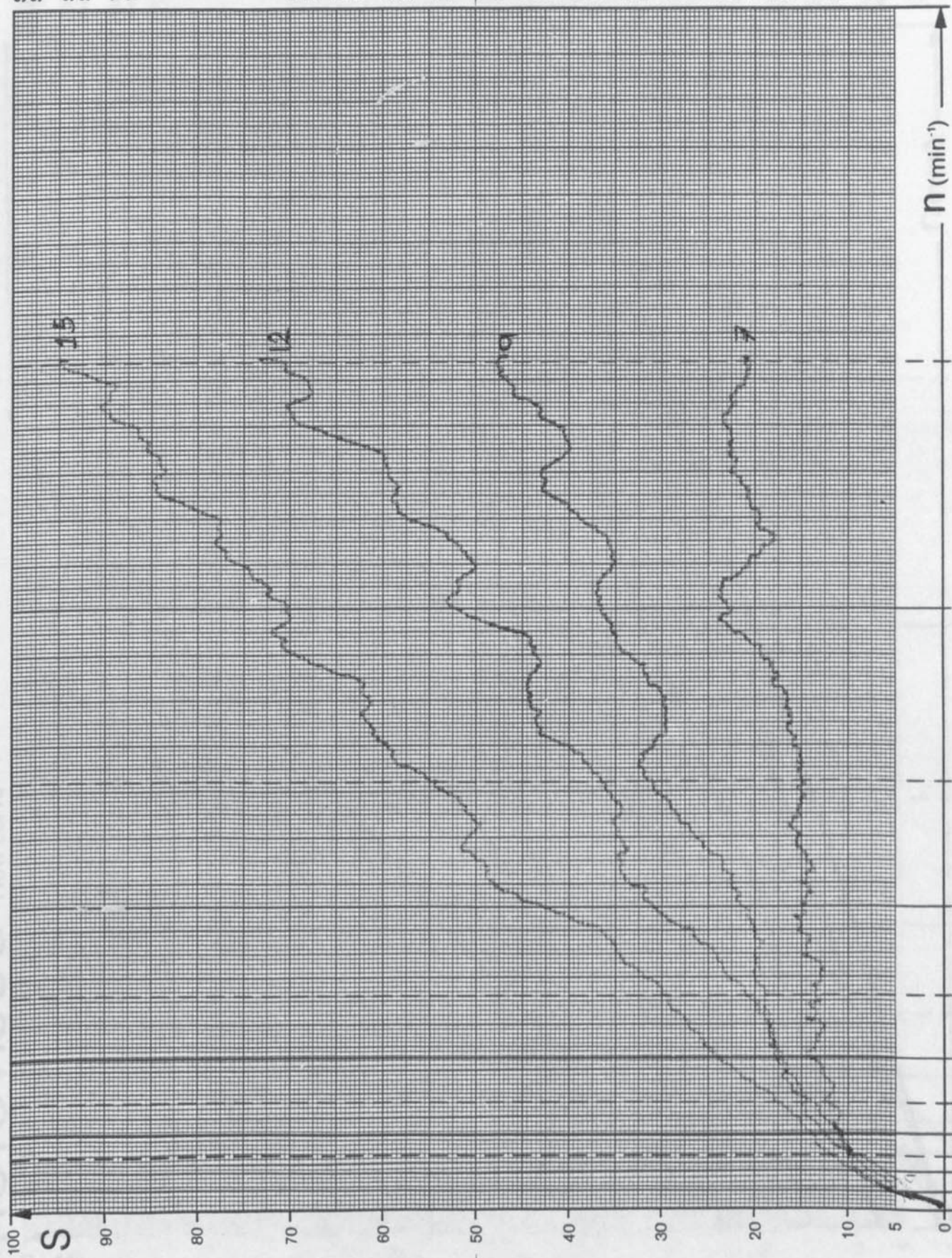
50
40
30
20
10
0



ROTOVISCO

Fließkurve
Flow curve

Speeds 7, 9, 12, 15 rpm
Ramp 1 min



Schubspannung $\tau = A \cdot S$ (Pa)
Shear stress
Schergeschw. $D = M \cdot n$ (s⁻¹)
Shear rate
Viskosität $\eta = \frac{G \cdot S}{n}$ (mPa)



Datum
Date 6/6/86
Nr.
No. 3
Substanz
Substance 1% CABOSIL
Temperatur
Temperature 23°
ROTOVISCO RV
Meßkopf
Measuring head CONED
PLATE
Meßeinrichtung
Sensor system
Faktor A
Faktor M
Faktor G
Programm
Program
Unterschrift
Signature

Bemerkungen:
Remarks: EFFECT OF 1% CABOSIL ON STANDARD SAMPLE AT DIFFERENT ROTATIONAL SPEEDS

ROTOVISCO

Fließkurve
Flow curve

Speed 10 /min
Time 30 sec.

Scale 3.2

Schubspannung $\tau = A \cdot S$ (Pa)
Shear stress

Schergeschw. $D = M \cdot n$ (s⁻¹)
Shear rate

Viskosität $\eta = \frac{G \cdot S}{n}$ (mPa · s)
Viscosity

1% CABOSIL



Datum
Date

Nr.
No.

Substanz
Substance

Temperatur
Temperature

ROTOVISCO RV

Meßkopf
Measuring head

Meßeinrichtung
Sensor system

Faktor A

Faktor M

Faktor G

Programm

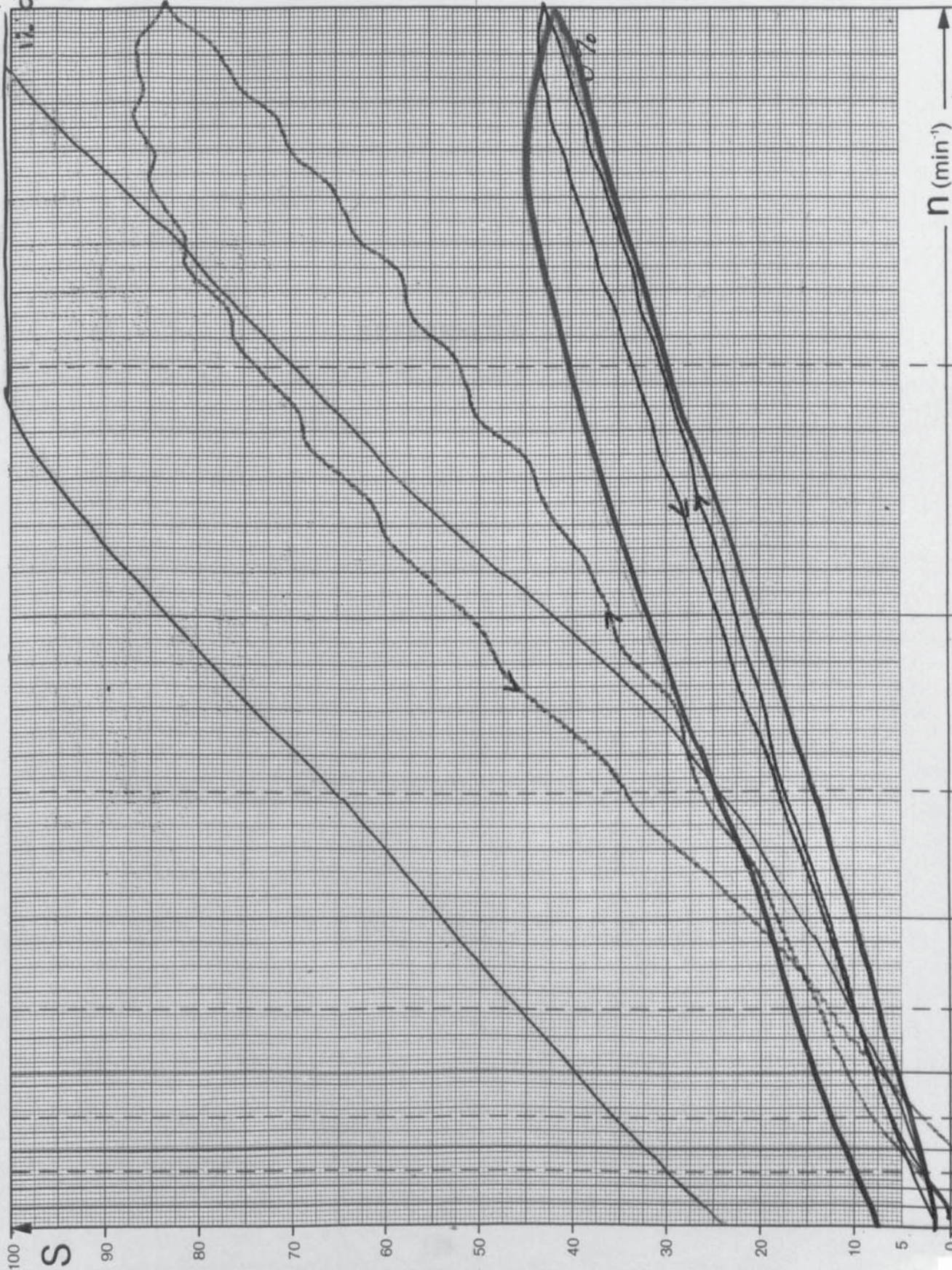
Unterschrift
Signature

Bemerkungen:
Remarks:

2nd graph is

4 mns after

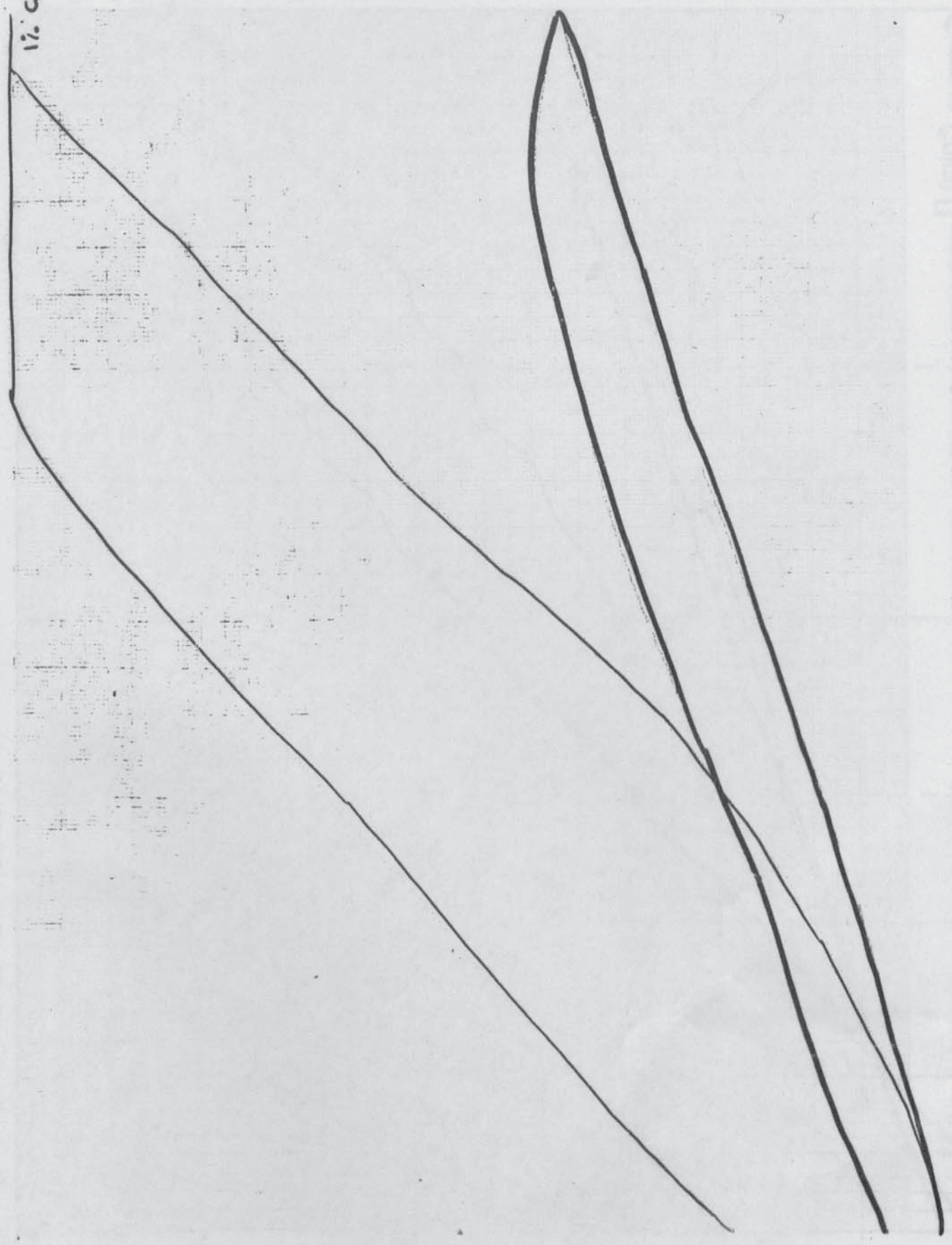
1st graph



Speed 10 /min
Time 30 sec.
Scale 3.3

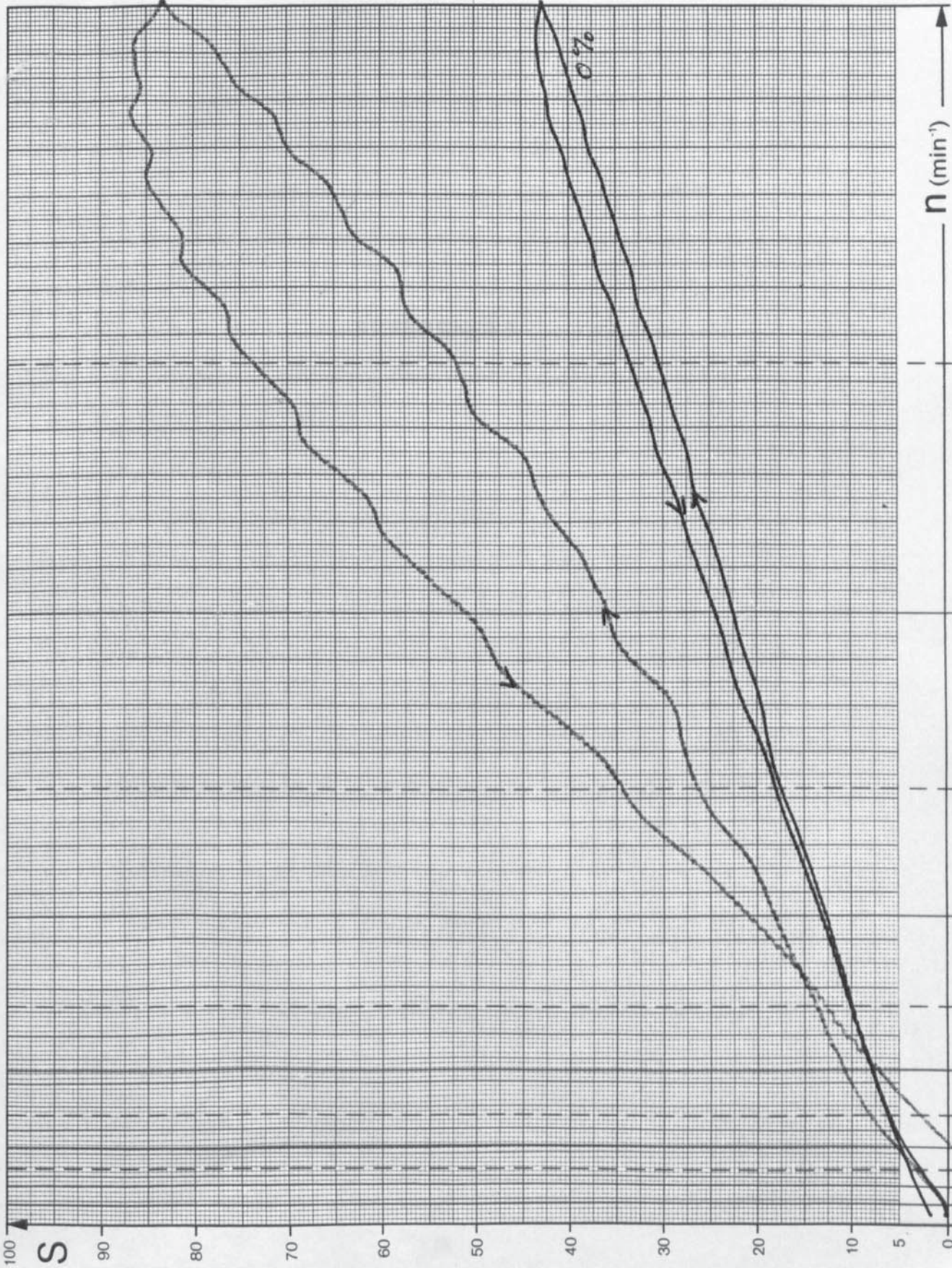
1% Cab.

0% Cab



ROTOVISCO

Fließkurve
Flow curve



Schubspannung $\tau = A \cdot S$ (Pa)
Shear stress
Schergeschw. $D = M \cdot n$ (s⁻¹)
Shear rate
Viskosität $\eta = \frac{G \cdot S}{n}$ (mPa · s)
Viscosity

1% CABOSIL



Datum
Date

Nr.
No.

Substanz
Substance

STANDARD
STANDARD
+ 1% CABOSIL

Temperatur
Temperature

ROTOVISCO RV

Meßkopf
Measuring head

Meßeinrichtung
Sensor system

Faktor A
Factor A

Faktor M
Factor M

Faktor G
Factor G

Programm
Program

Unterschrift
Signature

Bemerkungen:
Remarks:

2nd graph is
4 mns after
1st graph.

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