A Study of the Factors Affecting the Size Distribution of Microcapsules for Carbonless Copy Paper

By

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ABSTRACT

The process of micro-encapsulation by emulsifying a solution in a stirred tank has been accepted as the most suitable method for the production of microcapsules for carbonless copy paper and is currently used by Mondi Paper in Merebank. The focus of this project was to obtain a more uniform size distribution of the microcapsules so that oversize capsules would not smudge when they are coated on paper. There was also concern that the formation of very small ink/oil droplets was consuming wall material unnecessarily and was not contributing to the formation of an image on paper. The reduction of these tiny droplets would result in a saving of the cost of the wall material.

Mondi currently produces microcapsules with an average diameter between 4 and 5 microns. The amount of capsules produced above 10 microns, the oversize, is less than 1 per cent (v/v) and the amount of capsules produced below 2 microns, the undersize, is between 25 and 30 per cent. Mondi wishes to reduce the amount of undersize capsules, thereby producing a narrower size distribution. This could result in large savings, as discussed above. It could also lead to the production of a six-sheet set of carbonless papers instead of the four-sheet set, which is currently produced. The production of microcapsules by emulsification was investigated in a 2.5-liter laboratory tank, using an impeller measuring 45 mm in diameter.

A range of agitation speeds was investigated and it was seen that at the lowest speed that formed emulsions, 6600 rpm, 15.03 per cent of undersize capsules was produced and an average capsule diameter of 7.57 microns, after 40 minutes of agitation. At the highest impeller speed, 8000 rpm, the average capsule diameter was reduced to 1.93 microns and 67.02 per cent of undersize capsules were classified as "undersize". No oversize capsules were observed. These capsule specifications were not favourable. Further experimentation showed that at 7500 rpm, an average capsule diameter of 5.12 microns and an undersize of 24.20 per cent were observed. The proportion of oversize capsules was 1.63 per cent. Since these results were similar to the results obtained from the plant, 7500 rpm was used accepted as the "standard" speed for the experiments. A reduction in the impeller speed from 7500 rpm to 7200 rpm after the first 20 minutes of emulsification was one way on reducing the proportion of undersize particles further. The proportion of undersize particles

was reduced from 20.20 per cent to 19.71 per cent at standard conditions. The average capsule diameter and the oversize were not affected significantly.

The effect of the emulsification temperature on the particle size distribution was investigated with temperatures ranging from 22 to 40 °C, in increments of 2 °C. A temperature of 30 °C was used as a standard temperature as this temperature was being used at the plant. A decrease in the proportion of undersize capsules to 17.12 per cent was seen at temperatures below 30 °C and an average of 23.87 per cent was noticed above 30 °C. Although the proportion of undersize capsules decreased, the average capsule diameter increased beyond the specified range to an average of 7.77 microns at temperatures below 30 °C. At temperatures above 30 °C the average size was reduced to 5.59 microns. Hence the selection of 30 °C as the optimum temperature was confirmed.

Experimentation with the emulsification time showed that there were times when a unimodal size distribution was produced. However, these were at times just after the polymerisation had begun, and the reaction was not complete at this stage. A bimodal distribution was always noticed after 40 minutes of emulsification, i.e. after the completion of the reaction.

The effects of the baffle widths on the microcapsules were also investigated. Baffle sizes of 5, 10 and 15 mm were used. It was shown that with an increase in baffle width, there was a decrease in the amount of undersize capsules produced. However, the average capsule diameter became too large. A baffle width of 5 mm was shown to produce desirable capsule sizes, although the undersize did not improve, or worsen. Too much of air was trapped in the emulsion when no baffles were used in the tank.

Alternatives to the current surfactant, called "Lupasol" were tested so that Mondi could produce the capsules independently instead of relying on the original raw material supplier. This investigation was done based on limited information on Lupasol. Results from these experiments were inconclusive since more data on Lupasol was required.

Samples of the microcapsule emulsion were sent to different companies, in South Africa and abroad, to determine whether the particle size analyser used at Mondi was giving correct results. The results obtained from the companies in South Africa differed by a small amount from that measured at Mondi. However, results obtained from companies abroad varied considerably and it is recommended that Mondi change their particle analyser settings.

The power absorbed by the emulsion, in the laboratory-scale equipment was also found. This was determined by monitoring torque. The power was found to be 141.97 W and the power number was calculated as 0.357. It was noted that the power per unit volume in the laboratory equipment was significantly higher than the plant data (47 kW/m^3 vs. 12 kW/m^3).

The design of the impeller was not changed but the effect of baffle spacing was investigated.

PREFACE

The work presented in this thesis was performed at the University of Natal, Durban and Mondi Paper in Merebank, Durban, from July 2000 to February 2002. The work was supervised by Professor B.K. Loveday and Professor J.J. Marsh.

This thesis is presented in full requirement for the M.Sc. degree in Chemical Engineering. All the work presented in this thesis is original, unless otherwise stated and has not (in whole or part) been submitted previously to any tertiary education as part of a degree.

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Abbreviations

CB	Coated Back
CF	Coated Front
CFB	Coated Front and Back
DEA	Diethanolamine
DSD	Droplet Size Distribution
HLB	Hydrophilic Lipophilic Balance
MMD	Mass Median Diameter
NCR	National Cash Register
PIT	Phase Inversion Temperature
PVA	Polyvinyl Alcohol
SwRI	Southwest Research Institute

Notations

D	Diameter	m
F	Force	N
μ	Microns	mm
N	Impeller rotational speed	rps
Np	Power number	Dimensionless
O	Oversize capsules	%
P	Power	kW
ρ	Density	kg/m^3
r	Radius	m
Re	Reynolds number	Dimensionless
τ	Torque	N.m
U	Undersize capsules	%

V	Volume	m^3

CHAPTER 1

INTRODUCTION

Carbon paper was the earliest known and most widely used form of copying paper, with different varieties being available. Although it was ideally suited for the production of multiple copies of information on paper, it had several limitations. Toxicity of raw materials, disposal and ecological problems were some of the major factors affecting the use of carbon papers. It could also not be used in modern business machines, like electronic data processing equipment and computers. Business forms, like credit card forms, airline tickets and invoices couldn't be conveniently made with carbon papers. The increasing demand for modern business forms with multiple copies and the development of modern business machines, led to the growth of chemical carbonless copy paper.

Mondi Ltd. is the only company in South Africa manufacturing carbonless copy paper. It is produced at Merebank where Mondi Paper uses the BASF micro-encapsulation process to produce the microcapsules for the paper. Carbonless paper consists basically of two types of sheets. Coated on the back of the top sheet are the microcapsules, and coated on the top of the second sheet is a reactive clay layer. Figure 1.1 shows the basic structure of carbonless copy paper.

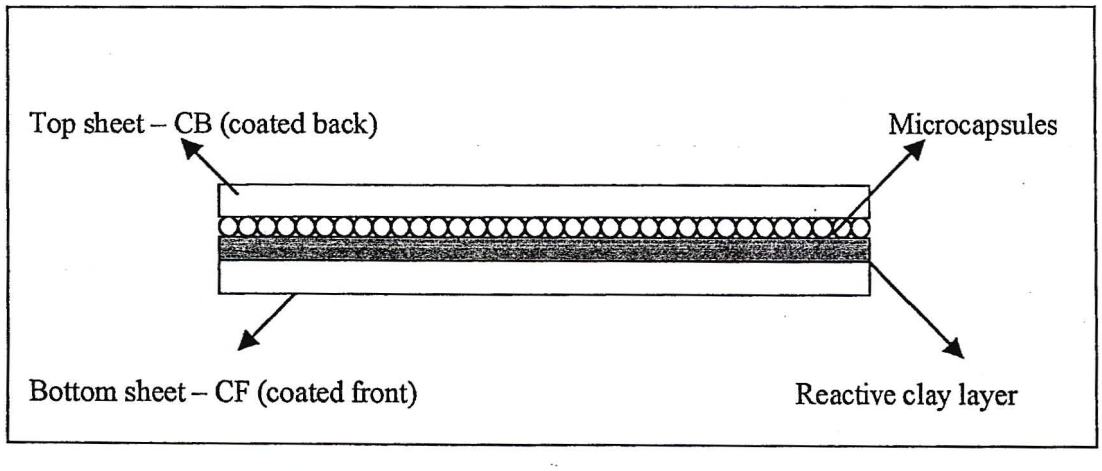


Figure 1.1: Structure of carbonless copy paper

1.1 Background

Two coated surfaces are involved in a carbonless copy system, one that acts as a donor or transfer surface and the other acts as a receiver or acceptor surface. Generally in a multiple copying paper set the papers are arranged in the form of CB, CFB and CF. The top sheet of a multiple copying set is called the CB (coated back) sheet, which is coated on the back side with micro-encapsulated dye. The middle sheet or CFB (coated front and back) sheet is clay coated on the top and the bottom side is coated with the micro-encapsulated dye. The last sheet or CF (coated front) sheet is clay coated on the top only, without the ability to transfer prints to additional copies. Figure 1.2 shows the arrangement of a multiple form set of carbonless copy paper.

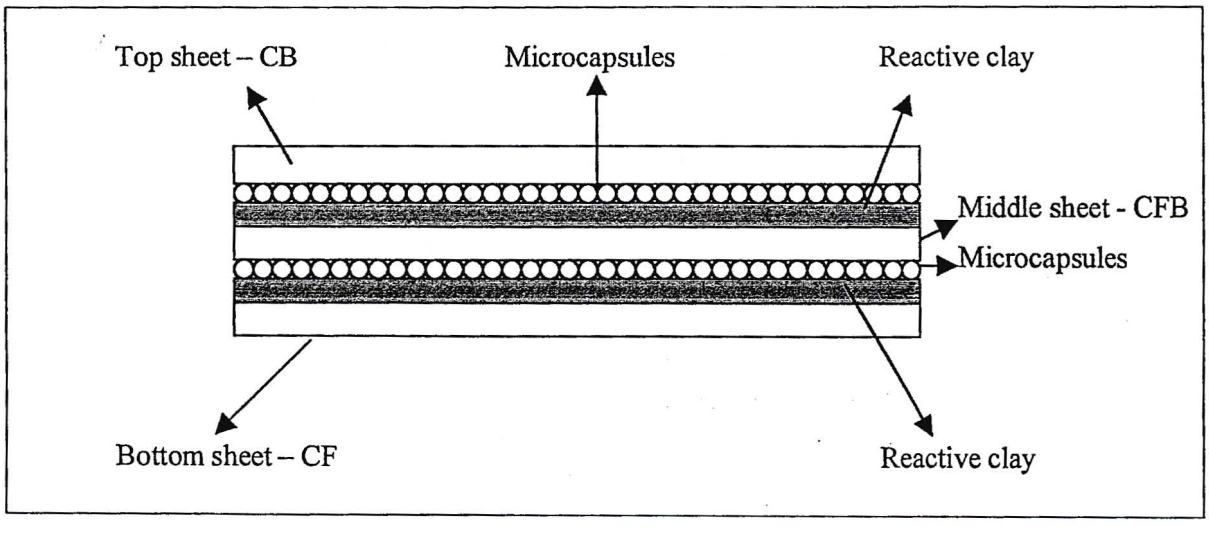


Figure 1.2: Structure of carbonless copy paper showing CB, CFB and CF

The film of microcapsules, which is coated on paper and dried, is rupturable by pressure. When localised pressure is applied, either by a ballpoint pen, pencil or by striking with the keys of a typewriter, the wall of the capsule is ruptured at the points of pressure. The colourformer ink stored within these walls is released onto the under-sheet, CF, and reacts with the layer of clay coated on it to produce an image. The clay used on the CF sheet is Silton clay, and various reactive clays can be used. Mondi Paper at Merebank presently has no problems with the clay used and production specifications are up to standard. The CB sheet however contains a few flaws since the process of micro-encapsulation is a very sensitive one. This project is focused on optimising the production of the microcapsules. Figure 1.3 shows the microcapsules coated on paper when viewed under an electron microscope.

Developments of the carbonless paper have shown that the two coating systems used may be incorporated on a single paper surface. The duplicating papers produced are termed "Self Contained record paper", or SC paper. Both the microcapsules and the Silton clay are coated on the same side of the sheet. SC papers are generally used for bank slips from ATMs and cash register receipts from supermarkets. Therefore improving the quality of the ink microcapsules would lead to a better quality of SC paper.

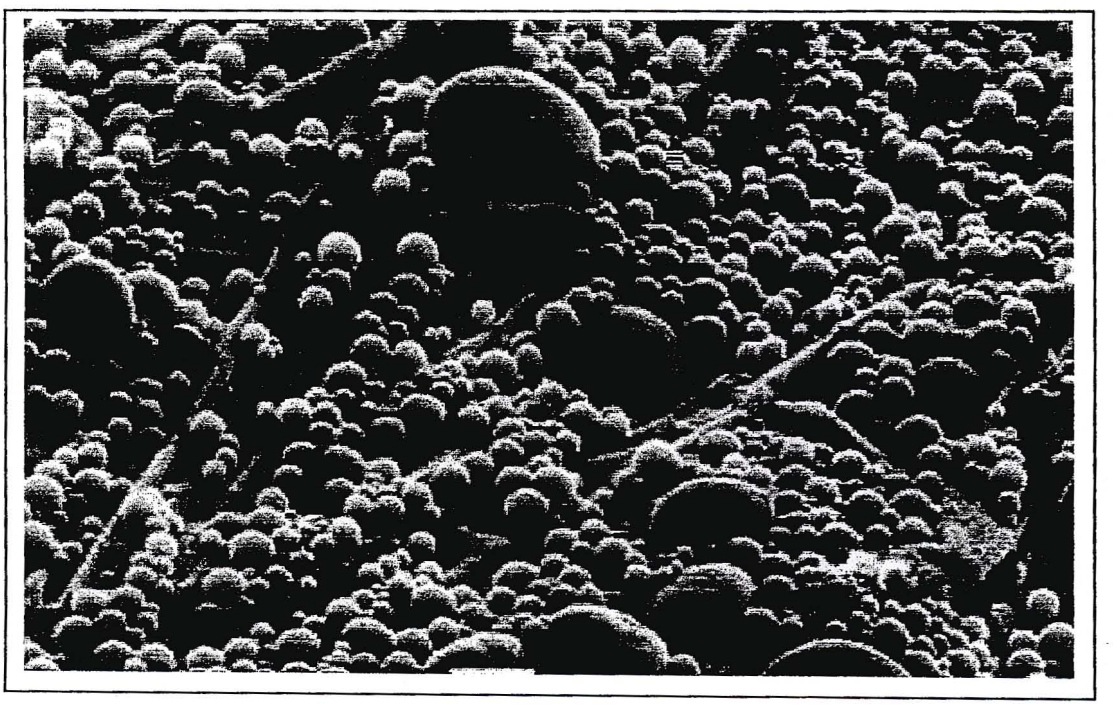


Figure 1.3: Microcapsules on paper viewed under an electron microscope (Tessmer [1999])

The long fibers seen in Figure 1.3 are the paper fibers, on which the microcapsules are coated. The very large spheres are starch granules, which serve as a buffer, preventing unnecessary rupture of the capsules.

Currently Mondi is able to produce a multi part set of up to four sheets of paper, which gives a clear and distinct image. Overseas competitors are able to produce up to six pages. This has caused concern at Mondi for two reasons:

- New customers would probably use the six-part carbonless paper set, from overseas companies, since Mondi's four-part paper set would be thought of as inferior.
- Some of Mondi's current customers, e.g. the shipping industry, require more than four copies of transactions.

Mondi initially produced the microcapsules using technology from Fuji, a Japanese based company. Three years ago, the BASF process was employed and since that time only a few minor adjustments have been made to the existing plant to accommodate the new process. There has been no technical support from BASF with regards to this new technology. As a result, Mondi has employed several consultants over the years, in order to gain a better understanding of the process. This MSc. project is also intended to shed some light on the process by allowing Mondi access to in-house technical support, instead of relying on BASF.

1.2 Mondi's microcapsule process

The current procedure for the production of the capsules consists of firstly forming the colourformer ink. This is done by mixing and heating the dye, Pergascript MC 28, and the solvent, Ruetasolv, at elevated temperatures. Water, capsule wall material (Luracoll), and a surface-active agent (Lupasol), is then added to the ink. After further mixing, formic acid is added to the solution to initiate the polymerisation reaction, which would encapsulate the ink using the Luracoll. After approximately an hour of emulsifying, using high-speed agitation, and after the particle size has been measured, the capsules are consolidated for about an hour. This involves agitating the solution at a moderate impeller speed, to improve homogeneity. Thereafter the capsules are hardened. The hardening procedure involves increasing the temperature of the emulsion and holding it for approximately 2 hours. The higher temperature allows the capsule wall to harden so as to protect it from bursting during normal handling of the paper. Once this is done the solution is cooled and prepared for storage. The rest of Section 1.2 describes the procedure in more detail.

1.2.1 Standard plant operating procedure

The amounts of reactants used during experimentation in the laboratory were in proportion to the amounts used at the plant. This was done since the system is sensitive to changes in the amount of reactants used, and could bring about an increase in the capsule size. Table 1.1 shows the amounts

used at the plant and at the laboratory for the production of the microcapsules. The functions of these reactants will be described in the following text.

Table 1.1: Amounts of reactants used at the plant and laboratory

Material	Plant (kg)	Laboratory (kg)
Pergascript MC-28	56	0.0280
Ruetasolv	1000	0.5000
Water	1178	0.5890
Lupasol	214	0.1070
Luracoll	231	0.1155
Formic acid	52	0.0260

1.2.1.1 Preparation of the colourformer ink

The first step in the production of the microcapsules is the preparation of the colourformer ink. The solvent, called Ruetasolv, is mixed with the dye, Pergascript, and then heated to about 105 °C. This mixture forms the colourformer ink. The ink is held at 105 °C for 30 minutes so that all the dye granules will dissolve. It is then cooled to 55 °C and filtered to remove any undissolved particles and dust impurities, which may have entered through the atmosphere. This is done before it is pumped into the emulsifier. It is important to remove any dust particles since it would be encapsulated, during the formation of the emulsion, resulting in wastage of the capsule wall material.

1.2.1.2 Preparation of the emulsion

The surfactant, Lupasol, the wall material, Luracoll and potable water are mixed thoroughly in the emulsifier for 10 minutes at 40 per cent of the maximum agitator speed (approximately 415 rpm). The agitator speed is then increased to 65 per cent (approximately 675 rpm) and the ink is pumped via a filter into the emulsifier. The contents of the emulsifier are then mixed for 15 minutes. Thereafter the agitator speed is increased to 75 per cent (approximately 775 rpm) and mixed for a further 10 minutes. The pH value of the emulsion must be between 3.6 and 3.8 for the polymerisation reaction to begin, and the addition of formic acid into the tank provides this. The addition of formic acid starts the formation of the capsule wall. After 40 minutes of high-speed agitation the agitator speed is decreased to 70 per cent (approximately 725 rpm) and a sample is

taken for particle size determination. At this point the desired capsule size may or may not be in the desired range. The emulsion is mixed for a further 20 minutes at 725 rpm if the size is not reached.

If the particle size is still above specification at this point, the emulsion is agitated further and samples are taken every 10 minutes until the desired size is obtained. Once the target particle size has been obtained, the speed is reduced to 60 per cent (approximately 620 rpm) and the batch is consolidated for 1 hour. The speed is reduced so that the capsules will not be broken down further by the high shearing action of the impeller. Thereafter hardening of the capsules begins.

A great deal of high-speed mixing occurs in the emulsifier and a large amount of energy is added to the solution in this way. In order to keep the temperature at a constant 30 °C, the emulsifier is cooled using cooling water, which passes through the steel jacket of the tank. When the speed is too high, suggesting a high temperature and therefore a high reaction rate, it is more difficult to achieve the desired capsule size distribution since the droplets are continuously being chopped up into smaller ones, by the high shear rate. The capsule wall may also not be as well formed as after a slower reaction. If the agitation speed is too low, the reaction proceeds too slowly and the capsules do not get broken down small enough to fall within the desired size range.

1.2.1.3 Hardening of the microcapsules

The contents of the emulsifier are then transferred to the hardening tank where the capsule walls will eventually harden. The batch is heated, by direct steam, to 75 °C and continuously agitated for 2 hours. The ventilation is switched on since a significant amount of formaldehyde is produced during this stage. During this time good agitation is supplied without introducing air into the batch since the air may be encapsulated. The agitation speed is also low enough to prevent the capsules from being broken down further. An impeller with a low shearing action is used during the hardening stage. Failure to supply sufficient agitation in this stage will solidify the entire batch. Even a short failure of mixing will result in formation of large clusters.

After 2 hours the batch is cooled to 50 °C and diethanolamine (DEA) is added into the tank. DEA stops the polymerisation of Luracoll by changing the pH to a higher value. After further cooling to 30 °C, Sterocoll and ammonia are added to the solution. Sterocoll serves as a lubricant and also adjusts the final viscosity to give a smooth flow behaviour to the coating ink. Ammonia adjusts the final pH of the solution. It also reduces the amount of formaldehyde produced in the ink during the

hardening step. The batch is finally mixed with starch, checked for quality and filtered into a storage tank. The starch serves as a buffer, which protects the microcapsules from being broken before use, i.e. by normal handling of the paper like packing, transporting and printing.

During the hardening step, steam is introduced directly into the batch to provide uniform heating. This steam condenses and adds to the water content of the batch. Therefore the amount of condensate is calculated beforehand and is deducted from the original amount of water in the recipe. If this is not done, the solid content of the final batch will be too low. Figure 1.4 illustrates a flowsheet of the microcapsule plant.

1.2.1.4 Particle size determination

During and after emulsification, samples are taken from the emulsifier to measure the average particle size. A few drops of the capsule sample are highly diluted and passed through a Malvern Mastersizer. The Mastersizer counts the number of particles in the sample and prints out the average volume diameter of the capsules, among other results. Figures A.1 to A6, Appendix A, shows typical printouts from the Mastersizer.

The experiments in the laboratory were aimed at optimising the size distribution of the capsules and since the capsule size is determined just after emulsifying, it was not necessary to conduct the hardening procedure.

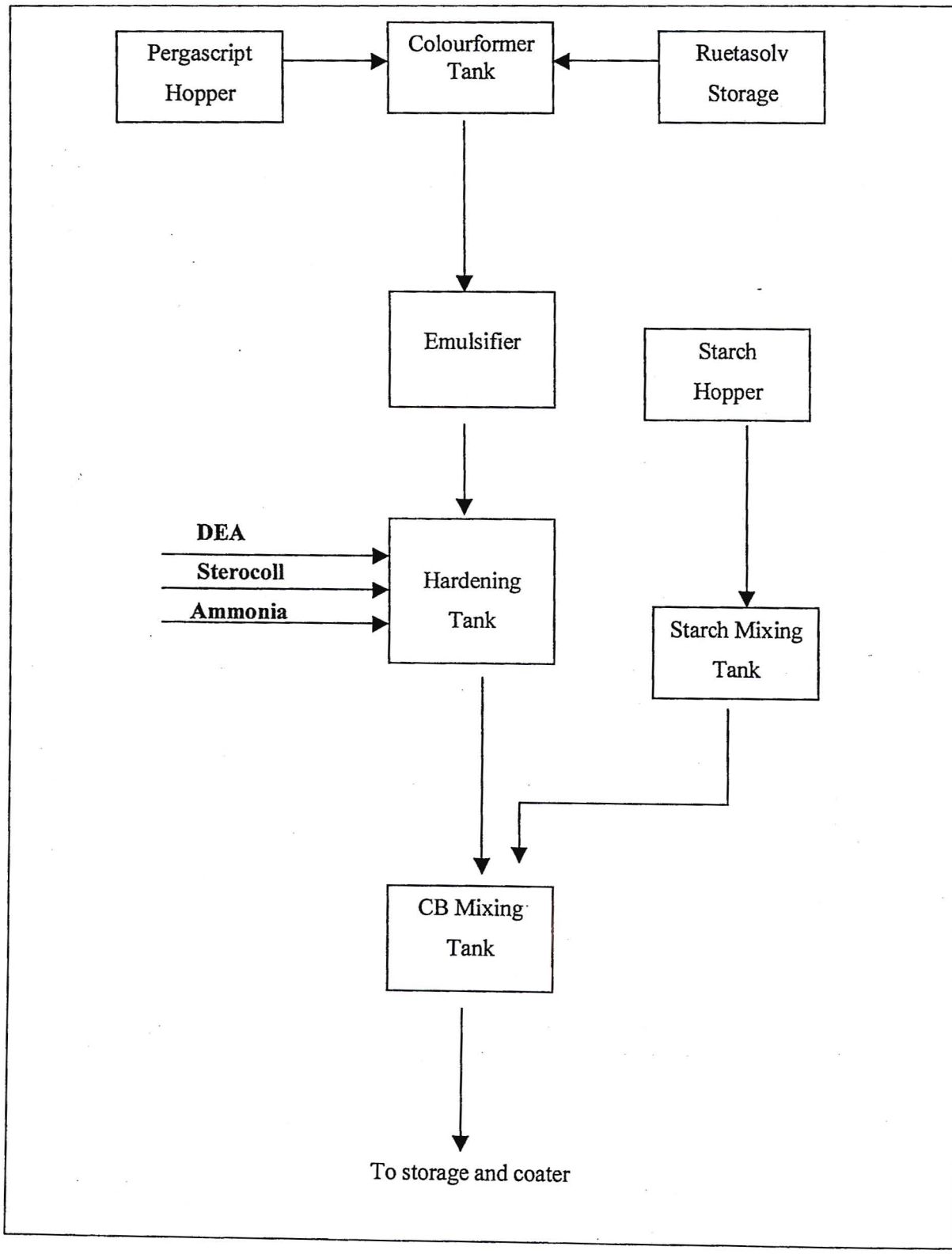


Figure. 1.4: Flowsheet of the microcapsule plant

1.3 Problems experienced on the CB sheet

One of the main problems experienced with the carbonless paper is blackening, or smudging, of the sheets during reeling, stacking and packing of the paper. This is caused by relatively large capsules, which break easily, thus releasing the ink within them. Another problem is the amount of ink released (intensity of the image). The reason for this is that some capsules are too small and don't have enough ink stored within them. As a result a clear image is not formed during writing, when the capsules rupture. This proportion of small capsules also influences costs, as additional material is used to encapsulate very little or no ink, resulting in wastage of the wall material. As a result of variations in capsule sizes, the paper produced sometimes does not meet the requirements of the customers, and are returned.

1.4 Project aim

The aim of the project was therefore to obtain a more uniform distribution of microcapsules, which would result in higher image intensity being produced. Currently Mondi produces microcapsules in the size range of 4 - 5 microns, which is ideal. Capsules that are 10 microns in diameter and greater are too large and currently Mondi is producing less than 1 per cent of the capsules greater than this size. Capsules that are less than and equal to 2 microns in diameter are too small, and currently about 25 to 30 per cent of the capsules produced by Mondi are below 2 microns. Ideally the proportion of capsules less than 2 microns should be as low as possible, preferably below 20 per cent. The proportion of oversize capsules (above 10 microns) and the average capsule diameter are currently within specifications and are not a problem for Mondi. However the proportion of capsules less than 2 microns, the undersize capsules, is too high. A saving of up to 20 per cent of the raw material could be made if the undersize fraction was reduced. The variables that affect the undersize capsules are:

- The agitation speed during emulsification
- The temperature of the emulsion
- Time taken for complete emulsification
- The type of agitator used
- The size of the baffles in the tank
- The chemistry of the surfactant used to produce the microcapsule emulsion.

In order to understand how the above variables affect the capsules and to bring about a successful decrease in the percentage of undersize capsules, an investigation of the optimal conditions for the production of microcapsules was conducted. This was done by studying the relevant literature on emulsification, surface-active agents and microcapsule manufacturing techniques. An investigation of the viability of a different surfactant was also done.

CHAPTER 2

A REVIEW OF THE THEORETICAL ASPECTS OF MICROCAPSULE MANUFACTURING TECHNIQUES AND EMULSION TECHNOLOGY

The invention of the micro-encapsulation technique has led to a breakthrough in the production of microcapsules for carbonless copy paper. Initially the capsules were produced by the process of coacervation from gelatin and gum arabic. Later developments have led to the capsules being produced by emulsification in a stirred tank, using the micro-encapsulation technique. In 1979, BASF invented the MICRONAL aminoplast process of producing microcapsules for carbonless paper. This process was successful in producing stable capsules, which are able to resist many climate conditions.

2.1 Background

Carbonless paper was first invented by the US Company, National Cash Register (NCR). Their name has become synonymous with the product "NCR paper", also known as "no carbon required paper." The convenience, cleanliness and attractiveness of carbonless copy papers have enabled them to penetrate the market for multi-part set forms. The low cost of raw materials and the technical and economic feasibility of recycling carbonless paper were also attractive features, which were not possible with carbon paper. The other advantages in using carbonless paper in the business environment include the following, according to Stadelhofer et al [1989]:

- No special, high-tech machinery or new skills were required for the printing of this paper.
- The readability of copies produced in computer printers was clearer and more distinct.
- The images produced were relatively free of smudges.
- The images were also not easy to erase and hence security was another justification for use of this paper.
- The quality of the paper did not deteriorate with time and repeated handling, as did carbon paper.

- The disposal of used paper and the unwillingness of staff to handle a dirty material were also major hurdles that were overcome.

In the early stage of development, carbonless paper chemicals, which produce colour on a reaction system, were merely coated on both sides of sheets of paper to produce carbonless copy paper. Many different chemicals were tried and tested but problems persisted. Poor quality images, smudging and oxidation of the dyes due to atmospheric exposure occurred frequently. The solution to all these problems was achieved by the introduction of the micro-encapsulation technique.

Micro-encapsulation can be best described as a micro-packaging technique that deals with packaging of various liquids, solids and gases in very small containers or capsules, which alter the requirements of application possibilities of a material (Saikia et al. [1980]). Broadly, micro-encapsulation provides a means of packaging, separating and storing materials on a microscopic scale for later release under certain controlled conditions. Minute droplets or particles of almost all materials can be enveloped in a uniform film of polymeric material and thus, isolated from reactive surroundings. The release of the encapsulated material can depend on different factors like the pH, moisture or temperature. In the case of carbonless paper it depends on the pressure, which is applied to the capsules, which ultimately bursts and release the dye stored within.

2.2 Emulsion theory

Microcapsules are extensively used in many industries such as pharmaceuticals, agrochemicals, paints, detergents, dry cleaning, and road applications (bitumen emulsions). Emulsions are a class of disperse systems made up of two immiscible liquids. One is the disperse phase and the second is the continuous phase (dispersion medium). The two most common types of emulsions are oil-in-water (o/w) and water-in-oil (w/o) emulsions, where the second phase is continuous. To disperse a liquid into another immiscible liquid, a third component, a surfactant, is normally added. The surfactant, also known as a stabiliser or emulsifier, helps in the emulsification process by adsorbing at the interface between the two phases. This results in the reduction of the surface tension and the formation of a protective layer around the oil drops, thus separating them. The emulsion is ultimately stabilised. In commercial practice the surfactant is often added to the continuous phase. In some cases though, dispersion of the surfactant in the dispersed phase may lead to smaller droplet sizes and more stable emulsions (Wan [1990], Brothman [1944] & Swern [1964]).

2.2.1 General considerations of emulsification

The stable form of an emulsion is obtained at the lowest free energy, when both the phases are continuous. Therefore the emulsion is said to "break" when it separates into two continuous liquid phases. Therefore the stability of an emulsion is measured by the rate at which droplets of the dispersed phase coalesce to form larger masses of liquid, which separate by gravity and form a separate bulk layer. There are two limitations on emulsions, one regarding particle size and the other regarding stability. In almost all emulsions, one of the liquid phases is aqueous and called the "water phase". The other is called the "oil phase", regardless of its exact chemical constitution (Sanchez et al. [1998]). The average particle size of the dispersed phase is a very important characteristic of emulsions. It is related to the rate of creaming, (the rate at which oil drops rise to the surface), and the rate of breaking, (coalescence of the dispersed particles), of the emulsion. A smaller particle size means a slower creaming rate, therefore a greater stability. The distribution of sizes, which is a measure of the uniformity of the particle size, is also very important. An emulsion, in which particle size is uniform, tends to be more stable than the ones with a wide size distribution. There is a dispersing-zone shear rate around the impeller, and there are coalescing-zone shear rates throughout the rest of the tank. The average shear rate in the tank is somewhere between the two zones. In making a stable emulsion, as in the microcapsule emulsion, it is usually the maximum impeller-zone shear rate, which is of interest since all the particles will eventually enter that zone (Oldshue [1983]). Since large particles, having a smaller phase boundary area per unit mass, are thermodynamically more stable than smaller particles, they tend to grow at the expense of small particles by coalescence. This phenomenon is called "Ostwald ripening" (Stenius [2000]).

When two globules of oil suspended in water collide, they will normally coalesce. When a surfactant is present, there will be relatively few instances of coalescence as compared with the number of collisions. The ratio of coalescence to collisions is an inverse measure of emulsion stability. This ratio is influenced by the nature of the protective film around each globule. It is also influenced by the violence of the collisions. The latter factor can depend on temperature, (a high temperature means more collisions since particles have higher energies), on agitation, on the charge of particles or on the viscosity of the medium (a high viscosity slows down the motion of the particles and therefore reduces the violence of the collisions). Stability also depends on the frequency of the collisions, which in turn depends on the phase volume ratio, temperature, electric charge, agitation and viscosity (Berkman & Egloff [1941]). Stability is usually measured by allowing an emulsion to stand under ordinary conditions of storage, and determining the time for it to break.

2.2.2 Formation of emulsions

An oil phase and a water phase must be agitated with surfactants in order to form an emulsion. The efficiency of emulsification depends, among other factors, on the type and degree of agitation, and the manner in which the surfactant is introduced (Gould [1959] and Vale & Taylor [1964]). The latter should be dissolved or dispersed in the oil phase and the mixture added, with stirring, to the water. Since most good o/w surfactants are more soluble in water than in oil, they will diffuse rapidly into the water phase and tend to promote dispersion of the oil. A less efficient method involves dissolving the surfactant in the water and then adding the oil phase with stirring (Schwartz [1949]). This method is used in some cases where intense agitation is required.

It was found that the most stable emulsions of the o/w type are formed when there are two surfactants, one of which is primarily oil-soluble and the other water-soluble. It was also found that no chemical reaction occurs between electrolytes and surface-active agents.

Oil in water emulsions, for some processes, can be obtained by either high-pressure injection of the oil into the tank, or by pouring the oil under high agitation. In the case of pouring the oil, Petela [1994], found that the droplet size diminished with a bigger impeller diameter and speed. In the case of oil injection, it was found that the droplet size diminished with a higher oil pressure. Other advantages of the injection method are:

- Due to reduced residence time, energy consumption for driving the impeller is reduced.
- The particle diameters are controlled by adjusting the pressure.
- The injection method allowed the reduction of the total processing time by about 80 per cent.

These advantages have been proven by experiments on a selective agglomeration of coal at a batch lab scale. A 76-micron orifice diameter was used at pressures ranging from 0.2 – 0.9 MPa. The diameters of the droplets obtained ranged from 0 – 200 microns.

Many different methods exist to produce emulsions. Uniqema, a division of ICI Surfactants has used the Emulsion Inversion Point (EIP) method as a preferred technique. In the EIP method the surfactant is first dissolved in the oil phase, instead of the current Mondi process where the water and surfactant are first mixed. The water phase is then slowly added to the oil/surfactant mixture under continuous stirring. In a first instance, a w/o emulsion is formed. The viscosity of this emulsion will increase sharply as more water is added and the emulsion reaches its

maximum viscosity at the inversion point. After reaching the inversion point, this w/o emulsion will now spontaneously invert into an o/w emulsion. The shear forces created by this viscosity increase are responsible for the creation of emulsion droplets of small and monodisperse particle sizes. The advantages of the EIP method over the more conventional direct emulsification method were summarized by Petela [1994] as follows:

- Possibility to achieve very low particle sizes i.e. < 250 nanometer
- Narrow particle size distribution
- Less foam generation
- Better long term stability

2.2.3 Emulsion stability enhancement

In order to obtain an optimum shearing effect in an emulsion, which is necessary for stability, there should be a low D/T ratio, where D is the impeller diameter and T is the tank diameter (Fondy & Bates [1963]). A surfactant is also crucial to ensure the stability of an emulsion. It accumulates around the dispersed phase droplets, forming an interfacial film, which prevents particle coalescence and flocculation. The addition of a second surfactant of a completely different nature lowers the interfacial tension even further. Not only is the quantity of the surfactant important, but also how fast it adsorbs, packs and orients at the interface. The molecular weight of the surfactant is also important in determining the size of the oil droplets produced in the emulsion (Wan [1990] and Griffin [1954]).

2.2.3.1 Surfactant concentration

A critical surfactant concentration exists above which the breakdown of the emulsion (flocculation or coalescence) would occur at an accelerated rate. An excess of surfactant in the emulsion results in the formation of micelles, which are small aggregates of surfactant molecules, usually spherical or rod shaped. This results in the separation of the surfactant-rich phases and eventually the formation of solid crystals (Tadros [1984]). These crystals are then encapsulated during the process.

2.2.3.2 Selection of surfactants

The presence of free surfactant in an emulsion may cause the system to flocculate, according to Bouillot et al. [1999]. Therefore it is important that the appropriate surfactant for a particular system is chosen. In order to make the selection of suitable surfactants easier, an attempt has been made to express the balance of the hydrophilic and lipophilic groups numerically. This is universally known as the hydrophilic lipophilic balance (HLB). An HLB value basically refers to how suitable a surfactant is for an emulsion. Generally a high HLB surfactant is used for o/w emulsions and a low HLB surfactant is suitable for w/o emulsions. Surfactants with a high HLB value disperse more readily in water, i.e. they are more hydrophilic, whereas surfactants with a low HLB value are more oil soluble, i.e. they are more oleophilic. The application of the HLB system is limited by the fact that the emulsion type is frequently also affected by other parameters e.g. water/oil ratio, temperature, viscosity (Falbe [1987]). Falbe found that many o/w emulsions with nonionic surfactants undergo a process of inversion to w/o emulsions at a certain temperature, the phase inversion temperature (PIT). The advantage of the PIT is that when such an emulsion is cooled rapidly, the reformation of the o/w system will have a smaller droplet size (Kerker [1975]). In practice, non-ionic surfactants are chosen for use at the PIT values, which are well above the typical storage temperature of the emulsion system. The particle size of an emulsion is ultimately manipulated by the choice of the surfactant (and/or blend), its concentration and the order of addition into the system.

2.2.4 Solvents

In the carbonless copying process, it is important that the writing on the paper develops within seconds, since a user will not want to wait for the image to develop. The solvents for the dye make an important contribution in this respect, according to Takashima et al. [1993].

According to Stadelhofer and Zellerhoff [1989], the solvents should meet the following requirements:

- The dye should be dissolved as quickly and completely as possible without being chemically altered or influenced.
- During the coating of the capsules, the paper is subjected to temperatures over 100 °C. The solvent should not evaporate at these temperatures since pressure would build up inside the microcapsules, causing them to burst prematurely.

- During the writing process, the dye must be transported immediately from the CB (coated back) page to the CF (coated front) page. The viscosity of the solvent should therefore not be too high.
- Once the dye solution has reached the surface of the CF page, the CF coating must be satisfactorily wetted; i.e. the surface tension of the solvent must not be too high and should be less than the surface tension of the CF coating.
- Once the copy colour has developed on the CF surface, it must not be transported away by the solvent, since the copy would "bleed" and become illegible. Accordingly, the solvent should have very little or no dissolving power for the developed dye.
- The viscosity of the solvent should also not be too low since this would lead to a "bleeding" effect.
- The solvent should be odourless to avoid annoyance to the users.
- The solvent should also be toxicologically safe so that the end user is not affected and the environmental pollution is avoided.

2.3 Micro-encapsulation theory

The first microcapsules were produced by the National Cash Register Corporation (NCR) using a process called complex coacervation. Fine droplets were first formed in an aqueous solution of a water-soluble polymer called gelatin, by high-speed agitation. Once the droplets had been formed, a second water-soluble polymer called gum arabic was added to the solution to initiate the coacervation reaction (Franjione & Vasishtha [1998]). Two incompatible liquid phases were formed. One phase, called the coacervate, has a relatively high concentration of the two polymers while the other phase, called the supernatant, has a low polymer concentration. The coacervate is the phase that contains the microcapsules. The capsules were then hardened. Microcapsule production by coacervation is still widely practiced today.

2.3.1 Southwest Research Institute (SWRI) encapsulation process

One of the many processes used at the SWRI for encapsulation is called the co-extrusion process. The liquid core and shell materials are pumped through concentric orifices, with the core material flowing in the central orifice, and the shell material flowing through the outer annulus. A shell, enclosing the core liquid is formed. The shell is then hardened by a chemical cross-linking agent. The size of the capsule and the quantity of the core material depend on the physical properties of the fluids. The co-extrusion process achieves a very narrow size distribution, but large capsules are produced, ranging from 1000 – 5000 microns (Franjione &

Vasishtha [1998]). This process is therefore not suitable to produce capsules for carbonless paper.

2.3.2 Microcapsule manufacture

In all of the patents studied a similar method for the production of microcapsules was noticed. Similar observations were also noticed. This Section summarises these patents, which are shown in Table 2.1. The method of capsule production can, not only be used for carbonless copy paper, but for other applications as well, such as microcapsules for perfumes, agrochemicals, and curing agents for adhesives. Most of these articles describe a process for producing microcapsules, for carbonless copy paper, by mixing the capsule contents in an aqueous solution and emulsifying the contents (Egawa et al. [1978], Fukuo & Onoguchi [1988]). The film around the oil droplets is formed by polymerisation. From all the patents studied a general approach to the production of microcapsules was noticed, which is summarised below. The differences noticed were the choice of reactants used and the different process variables, e.g. emulsion temperature and agitation speed.

Table 2.1: A list of the patents studied

1	Cook, E.J, and Lagace, A.P, *Apparatus for Forming Emulsions*, U.S. Patent 4533254, 1985.
2	Egawa, S, Sakamoto, M, Matsushita, T, *Process for Producing Microcapsules*, U.S. Patent 4082688, 1978.
3	Fukuo, H, and Onoguchi, T, *Microcapsule Manufacture*, U.S. Patent 4753759, 1988.
4	Pietsch, G, and Schrader, K.H, *Microcapsules and Microcapsule Production Process*, U.S. Patent 5011634, 1991.
5	Pietsch, G, and Schrader, K.H, *Microcapsules Containing Oils and Soluble Color Reaction Components, Their Manufacture and Use in Color Reaction Recording Systems*, U.S. Patent 4824823, 1989.
6	Scarpelli, J.A, *High Solids, Low Viscosity Carbonless Paper Gelatin Base Microcapsule System*, U.S.Patent 5064470, 1991.
7	Sodickson, L.A, *Apparatus for Producing Microcapsules*, U.S. Patent 4386895, 1983.

2.3.2.1 Claims made by patent literature

- A shortened manufacturing process of microcapsules is obtainable.
- A uniform capsule size is achieved.

- There is no deterioration of the dye.
- Good preservation stability is observed.
- There is an increased proportion of substance that is encapsulated without simultaneously increasing the viscosity of the solution to an unacceptable level.

2.3.2.2 Steps involved in the production of microcapsules.

The following steps refer to the microencapsulation process and are summarised from the different patents studied.

- Combining a hydrophobic oil, a cationic compound and an anionic sulphonated melamine formaldehyde precondensate (surfactant) in an aqueous medium.
- The oil is added under turbulence. A stable dispersion of oil is then formed
- The solution is acidified
- Contacting an aminoplast, wall-forming compound with the dispersed oil of acidified medium under laminar stirring conditions.
- The capsule shell is formed mainly by the condensation of the water-soluble, nonionic melamine formaldehyde precondensate (Benoit & Thies [1996]).

2.3.2.3 The process and some process conditions

A condensation reaction takes place during the subsequent formation of the capsule shell, which is acid catalysed. The optimum pH for the condensation reaction is in the weak acid range, between 3 and 6. Preference is given to 3.5 – 5.0. A high pH value increases the duration of the reaction. Low pH values should be avoided since it leads to undesired premature discolouration of the ink in the microcapsule. The anionic, water-soluble, melamine formaldehyde precondensate, reacted with the cationic reactant, gives the nonionic melamine formaldehyde precondensate which forms the capsule shell. It is also possible to add an ammonium salt to the reaction medium, e.g. ammonium chloride, which in some cases speeds up the condensation reaction. The invention can also be performed batchwise or continuously. To summarise, Table 2.2 shows a comparison between the microcapsules produced according to the different patent literature, and according to Mondi. Table 2.3 shows the differences in operation variables. The information was extracted from Tessmer [1999], Pietsch & Schrader [1991] and Scarpelli [1991].

Table 2.2: Comparison between the microcapsules produced by emulsification

Patent Literature	Mondi Process
1. Mixing of the colourformer ink and surfactant	1. Mixing of water, surfactant and wall material
2. Water added to the resulting solution	2. Colourformer ink added to the resulting solution
3. Solution is acidified	3. Solution is acidified
4. Wall material then added	4. Emulsification begins
5. Emulsification begins	

Table 2.3: Differences in operation variables produced by emulsification

Patent Literature	Mondi Process
Oil	Oil
1. Heat to 90 °C	1. Heat to 105 °C
2. Cool to 45 °C	2. Cool to 55 °C
Emulsification	Emulsification
1. Time ~ 40 to 60 minutes	1. Time ~ 40 to 60 minutes
2. Temperature ~ 20 to 30 °C	2. Temperature ~ 30 to 31 °C
3. pH ~ 3.5 to 4	3. pH ~ 3.6 to 3.8
Hardening	Hardening
1. Time ~ 2 to 3 hours	1. Time ~ 2 hours
2. Temperature ~ 60 to 70 °C	2. Temperature ~ 75 °C
3. Cooled to ~ 20 to 30 °C	3. Cooled to 30 °C
4. Final pH ~ 8.6 to 8.8	4. Final pH ~ 9.3 to 9.5

2.4 Methods for emulsion production and encapsulation

There are a number of laboratory and industrial scale processes for producing emulsions, which are widely practiced. Only a short summary of the most common process is given here.

2.4.1 Emulsification (dispersion method)

The formation of emulsions by breaking down a liquid into smaller particles in the presence of another liquid is achieved by mechanical means, i.e. by high shearing. In some cases, simple shaking or stirring may be sufficient. In other cases it may be necessary to apply very strong hydrodynamic forces as in commercial colloid mills. These mills cause the dispersion of a coarse mixture by shearing in a narrow gap between a static cone (the stator) and a rapidly rotating cone (the rotor) (Versic [1998], Vandegaer [1973]). Surfactants are necessary to stabilise the emulsion formed.

2.4.2 Interfacial polymerisation

This method involves the addition of a polymerisation initiator, an acid, to an emulsion of monomer droplets. Reaction between oil-soluble and water-soluble monomers at the oil-water interface of the dispersions can lead to interfacial polymerisation (White [1998]). The microcapsules produced are relatively uniform and its size is determined by the size of the monomer droplets.

2.4.3 Solvent evaporation

The first step in this process is to form a solution of polymeric wall material in a volatile solvent. The core material is then added to the polymer solution and the resulting mixture is dispersed in an immiscible liquid of lower volatility. The volatile solvent is allowed to evaporate thereby producing a suspension of solid particles (Alex & Bodmeier [1989] and Nihant et al. [1994]). This process normally produces ill-defined microspheres and is not suitable for carbonless paper production.

2.4.4 Coacervation

Coacervation, also called phase separation, was the technique developed in the 1950s by the NCR. It describes the phase separation of a liquid polymer-rich phase from a polymeric solution (continuous phase) when the solubility is reduced by some chemical or physical means. The core material is dispersed in the polymeric solution in which it is immiscible. A non-solvent, miscible with the continuous phase but a poor solvent for it will, under certain conditions, induce the polymer to form a coacervative layer around the dispersed phase. The capsules may

then be treated to give a rigid coat (Franjione & Vasishtha [1998] and Risch & Reineccius [1998]).

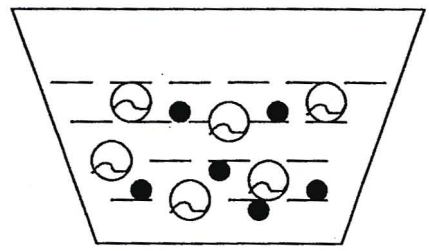
Coacervative encapsulation is a three-part process. It involves particle or droplet formation, coacervative wall formation and capsule isolation. Coacervation may be initiated in a number of different ways e.g. changing the temperature, pH or adding a second substance such as a concentrated, aqueous ionic salt solution or a non-solvent. Simple coacervation deals with systems containing only one colloidal solute, (e.g. only gelatin), while complex coacervation deals with systems containing more than one solute (e.g. gelatin and gum arabic). Coacervation is a very efficient but expensive method. Figure 2.1 illustrates this process.

2.4.4.1 Simple coacervation

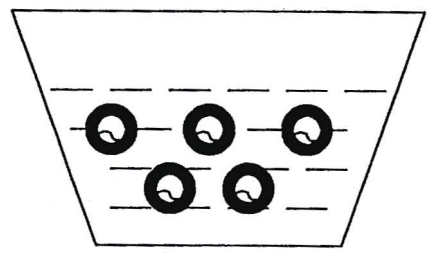
This process involves the use of either a second, more water-soluble polymer or an aqueous non-solvent for the gelatin. This produces the partial dehydration of the gelatin molecules at a temperature above its gelling point. This result in the separation of a liquid gelatin-rich phase in association with an equilibrium liquid, the gelatin-poor phase. Simple coacervation can be effected by either mixing two colloidal suspensions, one having a high affinity for water, or it can be induced by adding a strongly hydrophilic substance such as alcohol or sodium sulfate. An example of this process is explained as follows, according to Mussellwhite [1966]:

- To a 10% dispersion of gelatin in water, a core material is added under high agitation at a temperature of about 40 °C.
- A 20% solution of sodium sulfate or ethanol is added at 50 – 60% by final total volume to induce coacervation. There is continuous agitation throughout the procedure, which results in the temperature of the solution increasing.
- The emulsion is then cooled to 50 °C.
- The suspended coacervate capsules are insolubilised by adding a hardening agent, e.g. glutaraldehyde.
- Finally the pH is adjusted and the capsules are washed, dried and collected.

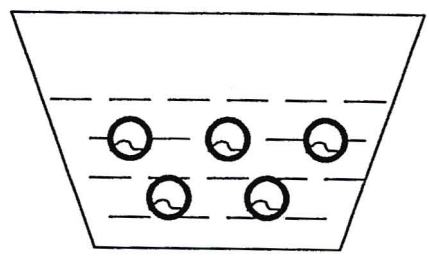
Step 1: Establishment of a three-phase system.



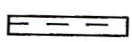
Step 2: Deposition of the liquid polymeric material



Step 3: Solidification of the wall material

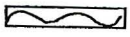


Phases:



Liquid vehicle

Coating material



Material to be coated

Figure 2.1: The different steps in a coacervation system

2.4.4.2 Complex coacervation

Complex coacervation is a common process used for microcapsule production for carbonless paper. It can be induced in systems having two dispersed hydrophilic colloids of opposite electric charges, e.g. gelatin and gum arabic. Neutralisation of the overall positive charges on one of the colloids by the negative charge on the other is used to bring about separation of the polymer-rich, complex coacervate phase (Luzzi & Gerraughty [1964]). The gelatin –gum arabic (gum acacia) system is the most studied system.

Complex coacervation is possible only at pHs below the iso-electric point of gelatin. At, or below, this pH gelatin becomes positively charged but gum arabic continues to be negatively charged. This results in the separation of the two phases by formation of capsule walls. Better results are obtained if the process is done at a slower pace. This process is explained as follows:

The core material is emulsified or suspended in either the gelatin or the gum arabic solution. The aqueous solution of gelatin and gum arabic should each be below 3% by weight.
The gelatin or gum arabic solution, (whichever was not previously used to suspend the core material), is then added to the system. The overall temperature of the system must be greater than the gelling point of an aqueous gelatin solution, (>35 °C). The pH is then adjusted to 3.8 – 4.3. There is constant mixing throughout the entire process, which results in the temperature of the system increasing rapidly. The system is then cooled to 50 °C and the gelled coacervate capsules are insolubilised by a hardening agent e.g. glutaraldehyde. The capsules are then washed, dried and collected.

2.4.5 Rotational suspension separation

This micro-encapsulation technique involves suspending core droplets in a pure coating material solution, then pouring the suspension through a rotating disk apparatus under such conditions that excess liquid between the core particles spreads into a film thinner than the core particle diameters (Cook & Lagace [1985]). The excess liquid is then atomised into very small particles that are separated from the product and recycled. The core droplets leave the disk with residual liquid still around them, which forms the coating. The particles are hardened by chilling or drying processes. Figure 2.2 illustrates the process.

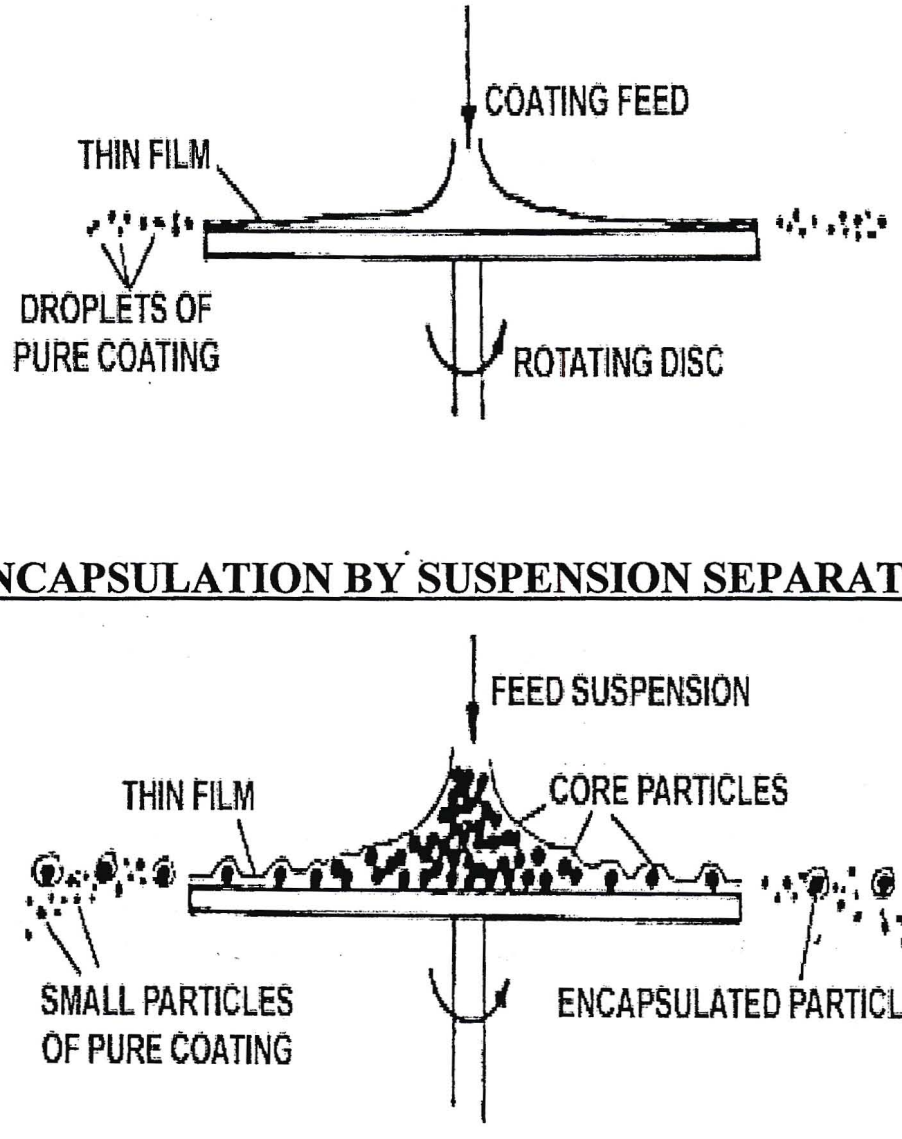


Figure 2.2: Rotational suspension separation process (Cook & Lagace [1985])

This is a continuous, high-capacity process that takes seconds to minutes to coat particles. It can handle a wide variety of core materials, including temperature sensitive cores. It can also handle coating materials in solid, liquid or suspension states, without presenting aggregation problems. Furthermore the process handles each particle only once and, under most conditions, produces no uncoated particles. The process has been used successfully to coat particles ranging from 30 microns to 2000 microns. Coatings have been produced with thickness ranging from 1 – 200 microns. Another advantage of this process is that the size distribution of the encapsulated particles resembles that of the uncoated particles.

The microcapsules produced at Mondi for carbonless paper, range in size from 1 to 10 microns. More specifically the ideal capsule size should be between 4 to 5 microns. This is a very narrow range to work with and since the rotational suspension method coats particles ranging from 30 microns to 2000 microns, it is not suitable for carbonless copy paper production.

2.4.6 The Wurster process

The Wurster process is a coating technique that is well suited to uniformly coat or encapsulate individual particles. This technology is characterised by the location of a spray nozzle at the bottom of a fluidised bed of solid particles. The particles are suspended in the fluidised air stream that is designed to induce a cyclic flow of the particles past the spray nozzle. The nozzle sprays an atomized flow of coating solution, which collides with the particles as they are carried away from the nozzle. This process is continued until each particle is uniformly coated to the desired film thickness (Sodickson [1983]). Figure 2.3 describes the Wurster method.

The advantages of the Wurster equipment are:

- Since the particles actually separate as they are carried away from the nozzle, it is possible to coat small particles without agglomeration.
- Particles ranging in size from fine powders to large particles, and including irregular shapes can be coated using this method.
- A wide variety of coating materials can be used including aqueous and organic solutions, lattices and dispersions.
- A uniform distribution of coating material is supplied among the particles in the batch.
- The equipment can be easily cleaned and assembled.

However this process is used to encapsulate solid materials with diameters ranging from 50 microns to several centimeters. It is therefore not suitable for carbonless copy paper production.

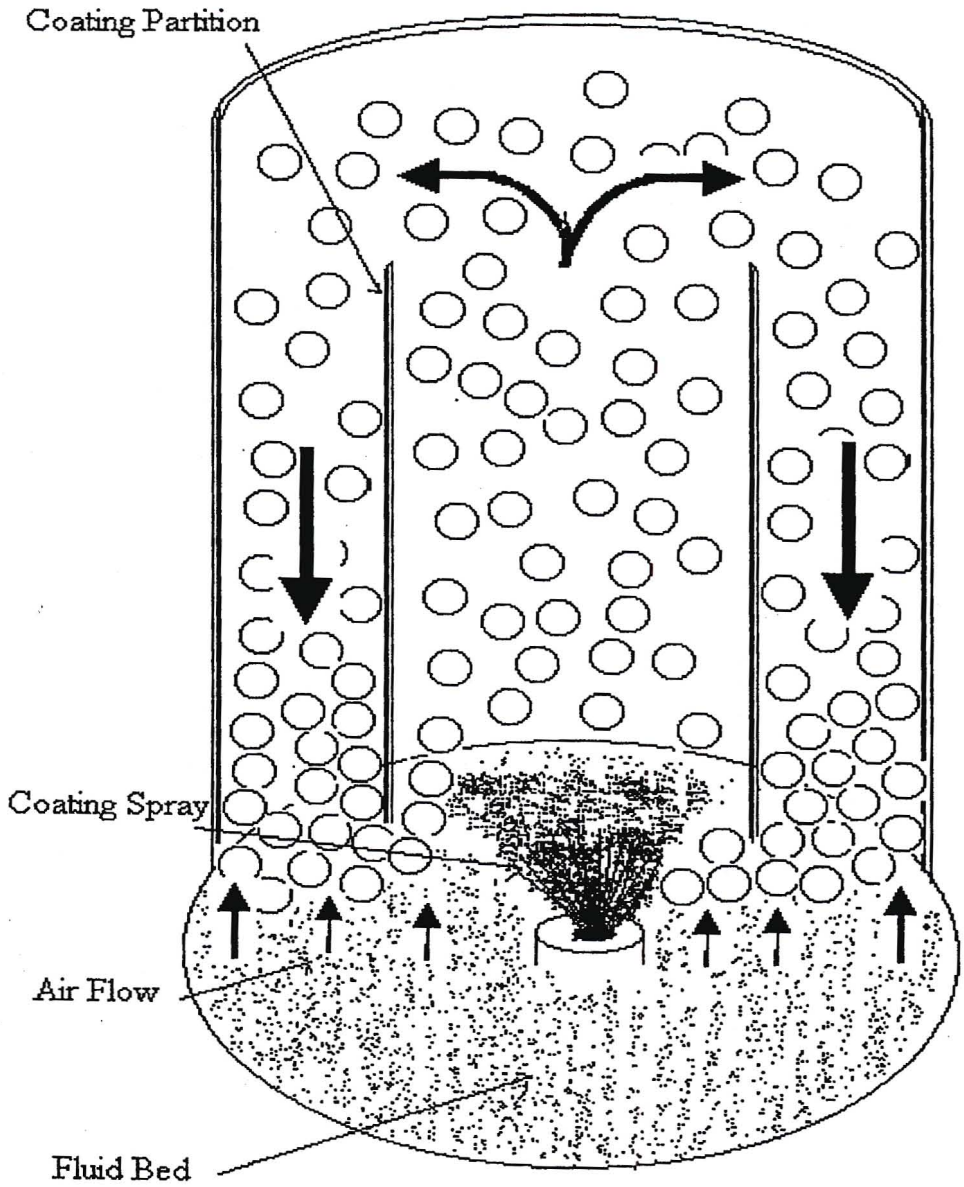


Figure 2.3: The Wurster process chamber (Sodickson [1983])

Considering the limitations of the production processes discussed, the emulsification method, which is currently being used at Mondi Paper, is the most suitable method for the production of microcapsules. This method also makes use of a polymerisation reaction that coats the capsules by a cross-linking process.

2.4.7 Micronal encapsulation technology

This method was invented by BASF, and is currently used by Mondi. It makes use of simple, efficient equipment and produces very stable capsules. The important chemicals in this process are the capsule wall forming material, Luracoll, and the water-soluble surfactant, Lupasol. Very little information is presently available on them since they are patented chemicals from BASF in Germany. A short description of how the process works is given below (Tessmer [1999]).

Luracoll, which is a melamine formaldehyde resin, has a high solids content (70%), and is able to form a durable, cross-linked structure.

An additional function of the resin, Lupasol, which is the protective colloid, is that it guides the liquid wall material to every fine droplet of oil, forming a completely closed film. In this way the ideal, round, fully closed microcapsules are formed. Figure 2.4 gives a breakdown of the steps involved in this process.

2.5 Comparison of the major encapsulation systems for carbonless CB coating

There are three primary types of encapsulation systems for the production of CB microcapsules. These are classified according to the material constituting the capsule wall and fall into three basic groups (Hoffman [1997] and Ichikawa [1994]):

- Gelatin capsules
- Polyurea (Isocyanate) capsules
- Melamine formaldehyde capsules (Mondi system)

Each system has certain advantages and disadvantages and a brief review on each process is given.

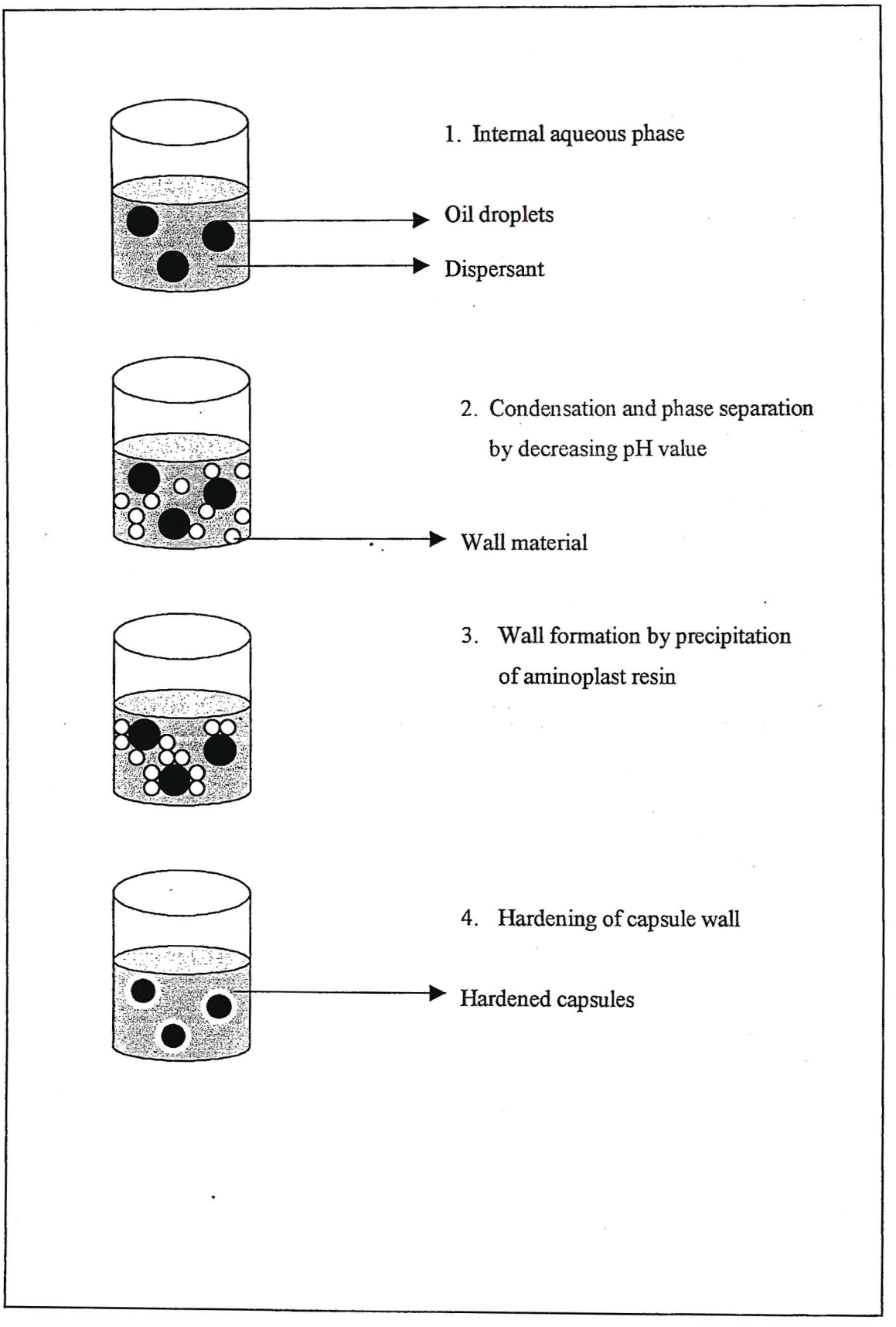


Figure 2.4: BASF Micronal encapsulation system

2.5.1 Gelatin capsules

Produced by a complex coacervation process, this system is widely used in Europe and North America. The main difficulty in this process is in the supply and handling of the gelatin wall material to achieve a consistent quality product. Being a natural product, the gelatin system is also prone to microbial attack.

The production process is relatively well known, but could be considered less robust than the other systems. Starch is often used as the binder.
Gelatin capsules generally have the largest size of approximately 10 microns, but exist mostly in the form of bunches as opposed to individual spheres. While this may promote good sheet coverage and high image density under low-pressure conditions or through multi part forms, image definition may be reduced.

2.5.2 Polyurea capsules

Produced by emulsification and interfacial polycondensation, this group includes polyurethane and polyamide wall materials. Again, the disadvantage of this system is the raw materials, which are usually polyisocyanates. Care should be taken when handling these products to avoid sensitisation of the skin. As the isocyanates polymerise readily in water or moist air, residuals in the coated sheet has never been a major issue.

The production of microcapsules by this process is straightforward and consistent. Either Latex or PVA is used as the common binders with this type of capsule.

The polyurea capsules are finer in size than the gelatin capsules at 6 – 7 microns. They may have stronger walls and better image definition. Low pressure during writing or multi part image density may be worse than the gelatin capsules. It may be possible to achieve a CB sheet of higher brightness with this system compared with the gelatin capsules.

2.5.3 Melamine formaldehyde capsules (Mondi system)

Produced by polymerisation, this group also includes urea formaldehyde and urea formaldehyde acrylic. This system is capable of the highest quality CB coating and has the finest capsule size of 4 – 5 microns. There is some concern over residual formaldehyde produced during polymerisation.

The production of these capsules is more complex than the other systems and requires greater process control. Synthetic binders are widely used in this system. Due to the finer particle size, these capsules are less prone to capsule damage and image smudging during handling.

2.6 Tank design

The tank design, with regards to the size and shape of the baffles, were also investigated. Before the results can be analysed, it is important to understand what occurs in the tank during agitation, since mixing forms an integral part of the microcapsule process.

There are two basic types of flow patterns that can be developed by mixing impellers, axial-flow or radial-flow. Axial-flow impellers produce flow parallel to the impeller shaft, along the impeller axis. Radial-flow impellers (the type used for the microcapsule process) discharge fluid to the vessel wall in a horizontal or radial direction. If suitable baffles are provided, a radial impeller will produce strong flow patterns from the radial discharge. If the vessel is unbaffled, swirling and vortexing may develop. This is undesirable, especially in the microcapsule process, since air may be encapsulated in the process.

Tank baffles

Axial-flow or radial-flow impellers in unbaffled tanks containing low viscosity fluids tend to swirl and produce vortices that are almost always undesirable. Installing baffles destroys the vortices and ensures that a homogenous, well-mixed emulsion is formed.

Baffles also improve the stability of an emulsion significantly, regardless of the type of impeller. The term "standard baffles" usually refers to four vertical baffles in a cylindrical tank, each of which is between one-twelfth to one-tenth the tank diameter in width, located 90° apart at the wall. The emulsion tank at the Mondi carbonless paper chemical plant has 3 baffles, which are triangular in shape. They are however, sufficient to prevent the formation of a vortex.

2.7 Scale-up of agitator speeds

In order to compare the speeds of a laboratory and plant scale impeller, it is necessary to use a scaling formula to determine the required agitation speeds. Since it is not possible to define the degree of agitation in quantitative terms there are two possible rules that one can use (Gibbon and Attwood [1962]).

The first assumes that the scale of mixing depends on the linear velocity at the tip of the agitator blades. Therefore the following equation can be used:

$$N_1D_1 = N_2D_2 \qquad (2.1)$$

Where N_1 is the rotational speed of the plant impeller, D_1 is the diameter of the plant-emulsifying tank, N_2 is the rotational speed of the laboratory impeller and D_2 is the diameter of the laboratory-emulsifying tank.

The second rule assumes that the degree of mixing is the same when the power input per unit volume of reactants is the same on both the plant and laboratory scales. The scaling rule is then:

$$N_1D_1^{2/3} = N_2D_2^{2/3} \qquad (2.2)$$

2.8 Power used in agitated vessels

In the design of an agitated vessel, an important factor is the power required to drive the impeller. Since the power required for a given system cannot be predicted theoretically, empirical correlations were developed to predict the power required (Geankoplis [1997]). The absence or presence of turbulence can be correlated with the dimensionless impeller Reynolds number, Re, defined as

$$Re = \frac{D^2 N \rho}{\mu} \qquad (2.3)$$

where D is the impeller (agitator) diameter in m, N is the rotational speed in rev/s, ρ is the fluid density in kg/m^3, and μ is the fluid viscosity in kg/m.s. The flow in the tank is laminar for Re < 10, turbulent for Re > 10^4, and for a range between 10 and 10^4, the flow is transitional, being turbulent near the impeller zone and laminar at remote parts of the vessel.

The power consumption in the mixing vessel is related to fluid density ρ, fluid viscosity μ, rotational speed N, and the impeller diameter D by plots of power number N_p versus Re. These plots should be similar for similar impeller geometries. The dimensionless power number is

$$N_p = \frac{P}{\rho N^3 D^5} \qquad (2.4)$$

where P is the power in J/s or W.

CHAPTER 3

EXPERIMENTAL

From information received from various analysts the size distribution of Mondi's microcapsules is too wide. Mondi also wishes to find an alternative surfactant to replace Lupasol, their current surfactant since it is expensive. Also, BASF holds the patent to Lupasol and they provide very little technical support when asked for help. Experiments were done at Mondi Paper in Merebank to try to rectify the size distribution problem and to gain a better understanding of the behaviour of the emulsion. An attempt has also been made to find a suitable alternative to Lupasol.

3.1 Experimental procedure

The desired particle size should lie in the range of 4 – 6 microns, with 99 per cent of the particles less than 10 microns. The proportion of particles less than 2 microns should also be as low as possible, preferably below 20 per cent. In order to meet these requirements, the following variables were investigated:

- The effect of agitation speed and time on average capsule size and the size distribution
- The effect of the emulsion temperature on average capsule size and the size distribution
- The effect of the baffle width on the average capsule size and the size distribution
- The use of a different surfactant

3.1.1 Modified laboratory operating procedure

It was essential to modify the operating procedure used at the plant in order to alter the necessary properties of the microcapsules. However only small changes were made since the process is very sensitive. Firstly the agitation speed required for the laboratory production of microcapsules had to be set. Since the emulsifier already available in the lab was not built to scale of the plant emulsifier, a proper method could not be used to determine the correct speeds required. Trial and error by a previous Mondi employee, who worked on the project, resulted in a fairly accurate estimate of the required speeds. The laboratory agitation speeds, which produced similar results, to that of the plant, were as follows:

Table 3.1: Plant and corresponding laboratory agitation speeds.

Plant motor power (%)	Plant agitator speed (rpm)	Agitator speed for both lab. tanks (rpm)
40	415	3270
60	620	6100
65	675	6600
70	725	7200
75	775	7500

The variables that were investigated were emulsion temperature, agitation speed, surfactant chemistry and basic tank design, with respect to tank baffles. During temperature variation experiments, only the emulsion temperature was changed. The rest of the procedure remained unchanged, with exception of the agitation speeds being changed to suit the laboratory emulsion.

Experimentation with the agitation speed refers to the speed during the emulsification process, i.e. after the addition of formic acid into the emulsifier. Instead of emulsifying at 7500 rpm, the speed was changed to 8000, 7200 and 6600 rpm. For the experiments involving the tank design the changes made were, increasing the size of the tank and changing the baffle size. The increase in

size also allowed for experimentation with larger baffle sizes, including 5 mm, 10 mm and 15 mm. The outcome of these experiments is discussed in Chapter 4.

3.1.2 The Emulsion Inversion Point method

As discussed in Chapter 2 there exists a unique method of producing stable emulsions, called the Emulsion Inversion Point (EIP) method. Claims had been made by Uniqema, a division of ICI Surfactants, that this method produces an emulsion with a narrow size distribution. The EIP method was therefore tested and the following changes to the normal operating procedure was made:

- Instead of mixing the water, Lupasol and Luracoll together, the colourformer oil, Lupasol and Luracoll was mixed for a period of 10 minutes.
- Formic acid was then added the solution and agitation was continued for a further 10 minutes.
- Thereafter, water was slowly added over a period of 5 minutes, and the viscosity of the emulsion began to increase. This allowed the inversion from a water-oil emulsion to an oil-water emulsion.
- Once all the water was added, the emulsion was further agitated and tested for particle size as done previously.

These experiments were done in a new tank, which had been scaled down in size, from the plant tank to exactly one-tenth. An emulsification temperature of 30 °C and a constant agitation speed of 7750 rpm were used, in keeping with the scale-up rule of Equation 2.1, Chapter 2. The experiments were repeated to ensure the consistency of the results, which can be seen in Chapter 4.

3.1.3 Experimentation with different surfactants

The chemical Lupasol is a highly specific surfactant and is very well suited for the microcapsules. However the performance of similar chemicals were investigated, with a view to providing Mondi with alternatives.

3.1.3.1 Determining the "Required HLB" value for the microcapsule emulsion

In order to find a surfactant, which performs a similar function to that of Lupasol, it was necessary to first determine the HLB of the microcapsule emulsion. This is called the "Required HLB" of the emulsion, or oil. The method used involved producing a series of trial emulsions and blending them with surfactant combinations of known HLB values. A combination of two or more surfactants generally produces a much more stable emulsion than using a single surfactant. The surfactants used for these trials were:

- Span 80 (HLB of 4.7)
- Tween 80 (HLB of 14.9)
- Tween 20 (HLB of 16.7) and
- Myrj 59 (HLB of 18.8)

These are all water-soluble surfactants and were chosen because of the large variation in their HLB values. The surfactant combination that works the best, i.e. the combination that shows the best dispersion of oil droplets in the solution, is the one with the HLB value equal to the "Required HLB" of the emulsion (Takahashi et al. [1993]). The procedure for this process involved the following:

- Small batches of seven surfactant combinations, ranging in HLB values from Span 80 to Myrj 59 were made as shown in Tables 3.2 to 3.5.

- Seven test emulsions were made, each using one of the surfactant samples. Due to a small quantity of surfactant available the volume of oil used was 10 ml. The oil was initially heated to 105 °C, and then cooled to 55 °C as done in the plant at Mondi.
- The amount of surfactant added was 15 per cent of the oil volume. Ideally, 10 – 20 per cent of the oil volume should be added. No water was necessary as these tests were only used to show how well the surfactant disperses the oil.
- The surfactant was then dissolved in the oil with agitation.
- After the emulsion was produced, the most stable and well-dispersed emulsion was judged visually.
- Where all the emulsion samples showed fairly good droplet dispersions, but not much noticeable difference between them, they were to be repeated using a smaller amount of surfactant.
- If the samples had poor droplet dispersions, but no great difference between them, they were repeated using more surfactant.

Table 3.2: Surfactant blends used in making trial emulsions

Sample number	Surfactant blend (%)		Calculated HLB
	Span 80	Tween 80	
1	100	0	4.7
2	87	13	6.0
3	68	32	8.0
4	48	52	10.0
5	28	72	12.0
6	6	94	14.0
7	0	100	14.9

Table 3.3: Surfactant blends used in making trial emulsions

Sample number	Surfactant blend (%)		Calculated HLB
	Tween 80	Tween 20	
1	100	0	14.9
2	87	13	15.1
3	68	32	15.4
4	48	52	15.8
5	28	72	16.1
6	6	94	16.5
7	0	100	16.7

Table 3.4: Surfactant blends used in making trial emulsions

Sample number	Surfactant blend (%)		Calculated HLB
	Span 80	Tween 20	
1	100	0	4.7
2	87	13	6.2
3	68	32	8.5
4	48	52	10.9
5	28	72	13.3
6	6	94	15.9
7	0	100	16.7

Table 3.5: Surfactant blends used in making trial emulsions

Sample number	Surfactant blend (%)		Calculated HLB
	Span 80	Myrj 59	
1	100	0	4.7
2	87	13	6.5
3	68	32	9.2
4	48	52	12.0
5	28	72	14.8
6	6	94	17.9
7	0	100	18.8

3.1.3.2 Determining the HLB of Lupasol

Once the "Required HLB" of the emulsion was found, it was necessary to determine the HLB of Lupasol, the current surfactant used at Mondi. This value was not available in product literature and it was measured since it is required when selecting new surfactants. To get a rough idea as to what range the HLB value lies in, the water solubility method was used. Table 3.6 summarises this method. The HLB range found after conducting the water solubility method was above 13, which confirmed that a hydrophilic surfactant was needed.

The exact HLB value of Lupasol was then measured. The method used consisted of blending Lupasol in varying ratios with each of the above surfactants. The resulting blend was then used to emulsify the oil with the known "Required HLB." The blend that had the best visual dispersion of droplets was assumed to have an HLB value approximately equal to the "Required HLB" of the oil. The HLB of Lupasol was then easily calculated. The results can be seen in Chapter 4.

Table 3.6: The water solubility of Lupasol (Griffin [1954])

HLB by dispersibility	HLB range
No dispersibility in water	1 - 4
Poor dispersion	3 - 6
Milky dispersion after vigorous agitation	6 - 8
Stable milky dispersion	8 - 10
Translucent to clear dispersion	10 - 13
Clear solution	13 +

3.1.3.3 Trial of new surfactants

Based on the calculated HLB, alternatives to Lupasol were tested. The operating procedure and conditions remained the same as a normal run, with the exception of Lupasol being replaced by the new surfactants. The outcome of the experiments is discussed in Chapter 4.

3.2 Experimental equipment

The equipment used was already available at Mondi and consisted of the following:

- A laboratory emulsifier for the production of the microcapsule emulsion.
- A Silverson mixer for the agitation of the emulsion, model L2R
- A heater and agitator for the production of the colourformer ink.
- A Malvern Mastersizer for the particle size analysis, model MAF5000/1

3.2.1 The laboratory emulsifier tank

The mixing vessel used in the laboratory was a stainless steel tank, 108 mm in diameter, 240 mm high and filled to a height of approximately 135 mm. The vessel was equipped with three equally spaced baffles, 5 mm in width and 120 mm high. Figure 3.1 shows a picture of the tank, and its dimensions can be viewed in Figure 3.2. A Silverson mixer with a variable speed motor drove the impeller that was located 2 cm above the base of the tank. The impeller was a high shear, turbine impeller, 45 mm in diameter and 11 mm thick. Figures 3.3 and 3.4 show the agitation equipment used, including the Silverson mixer and the impeller.

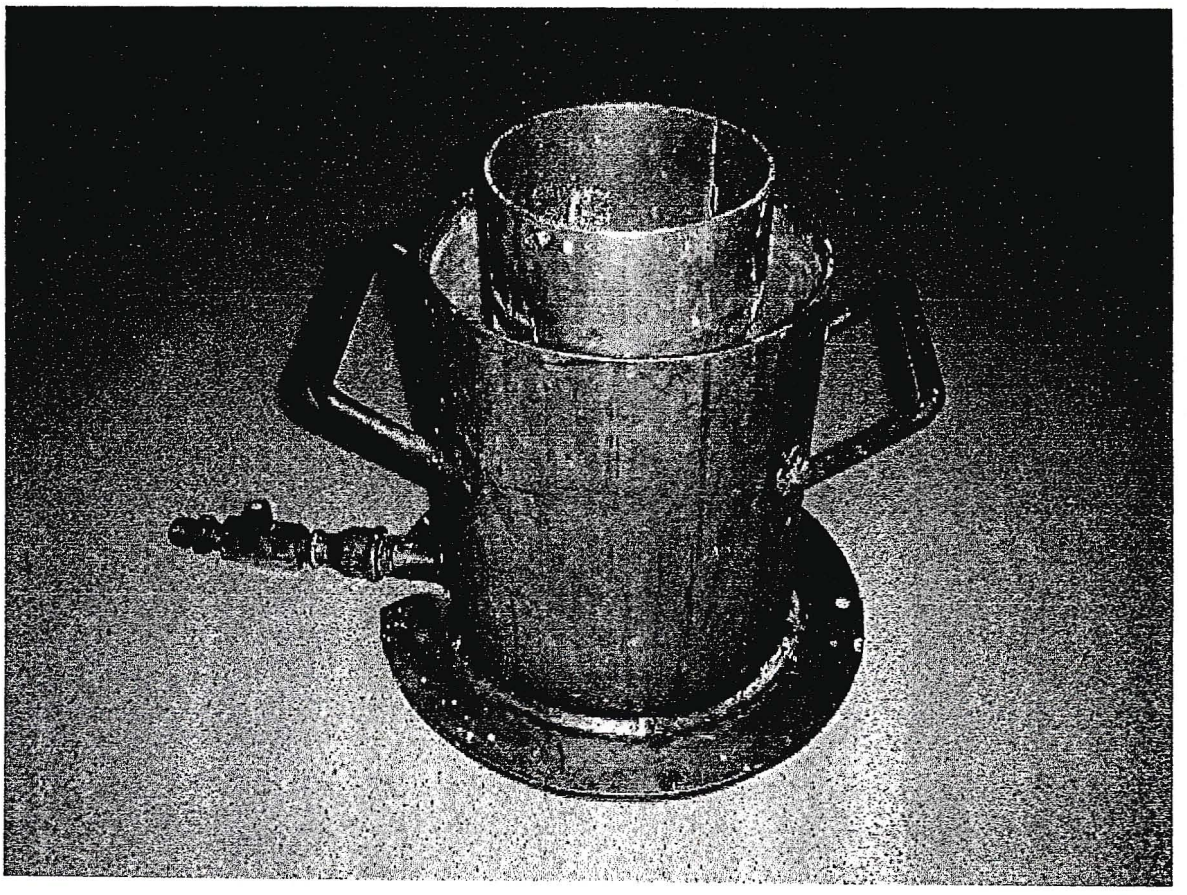


Figure 3.1: Laboratory emulsifier tank

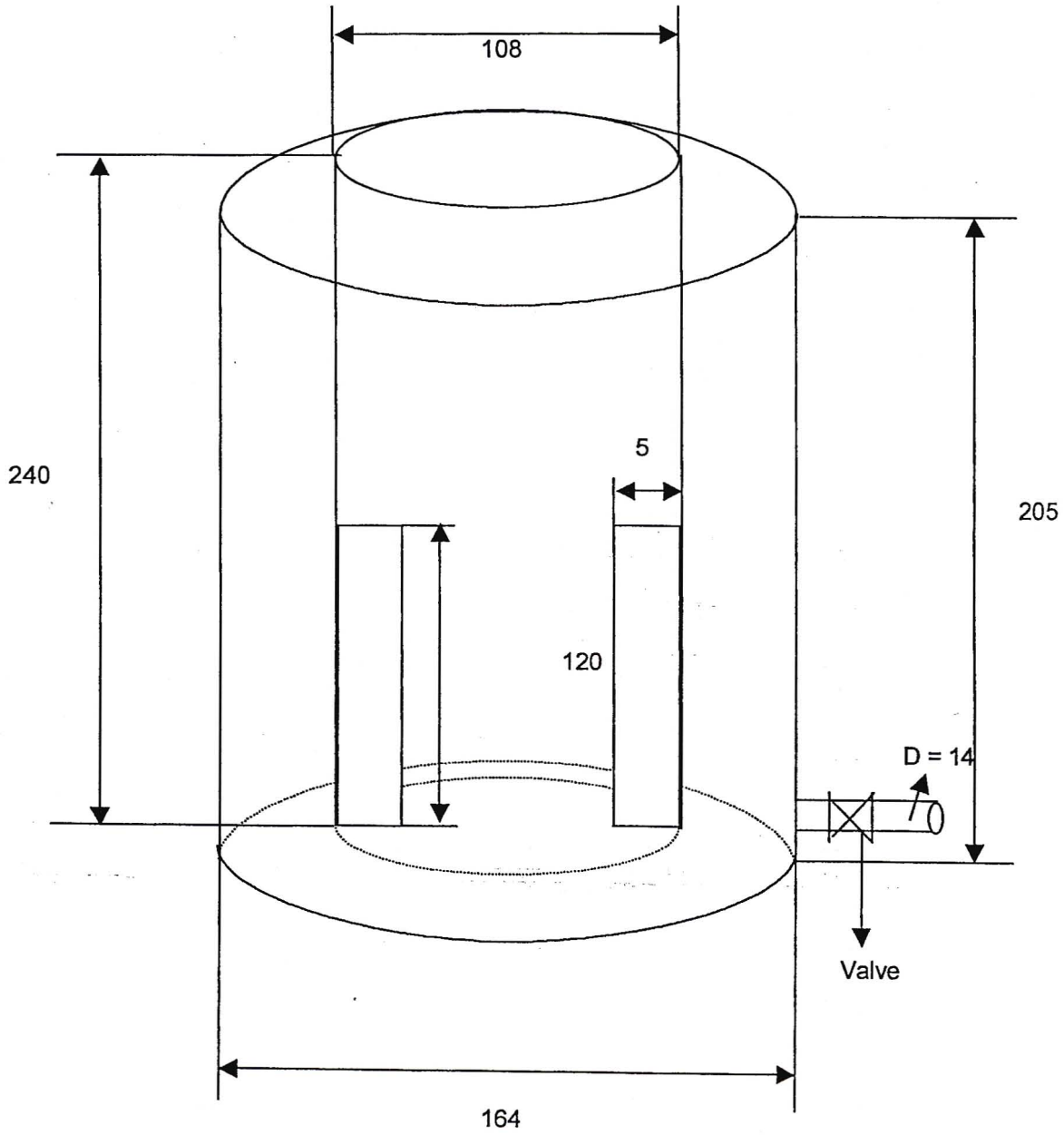


Figure 3.2: Laboratory tank with dimensions

Inner tank
Diameter = 108 mm
Height = 240 mm
Outer tank
Diameter = 164mm
Height = 205 mm
3 baffles
Material: stainless steel
Outlet pipe: Diameter = 14 mm

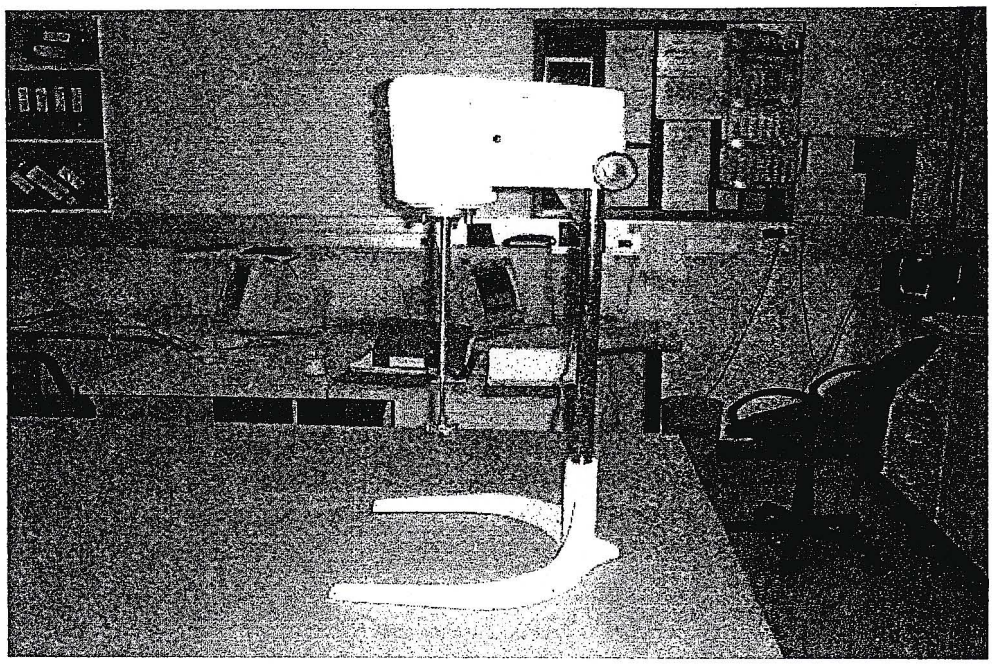


Figure 3.3: Silverson mixer

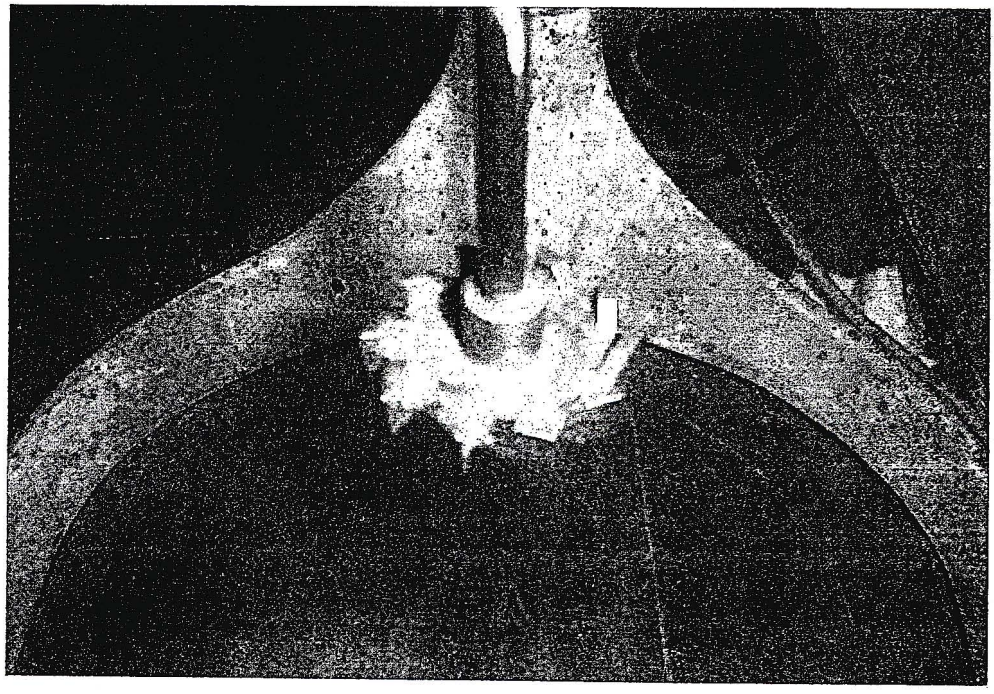


Figure 3.4: Laboratory impeller

The equipment used was the existing equipment available at Mondi and it was constructed to simulate similar conditions as the plant. However the laboratory tank was not made to scale of the plant tank. A new laboratory tank was also constructed, from perspex, to conduct the baffle size-variation experiments. The widths of the baffles used were 5, 10 and 15 mm. The can be seen in Figure 3.5. The two laboratory tanks have an external compartment, which is used to control the temperature of the emulsion. A large amount of heat is generated by the high impeller speeds, which is transferred to the emulsion. Since the emulsion is very sensitive to temperature, which can affect the outcome of the experiment, cold water was added to the external jacket, to keep the temperature constant.

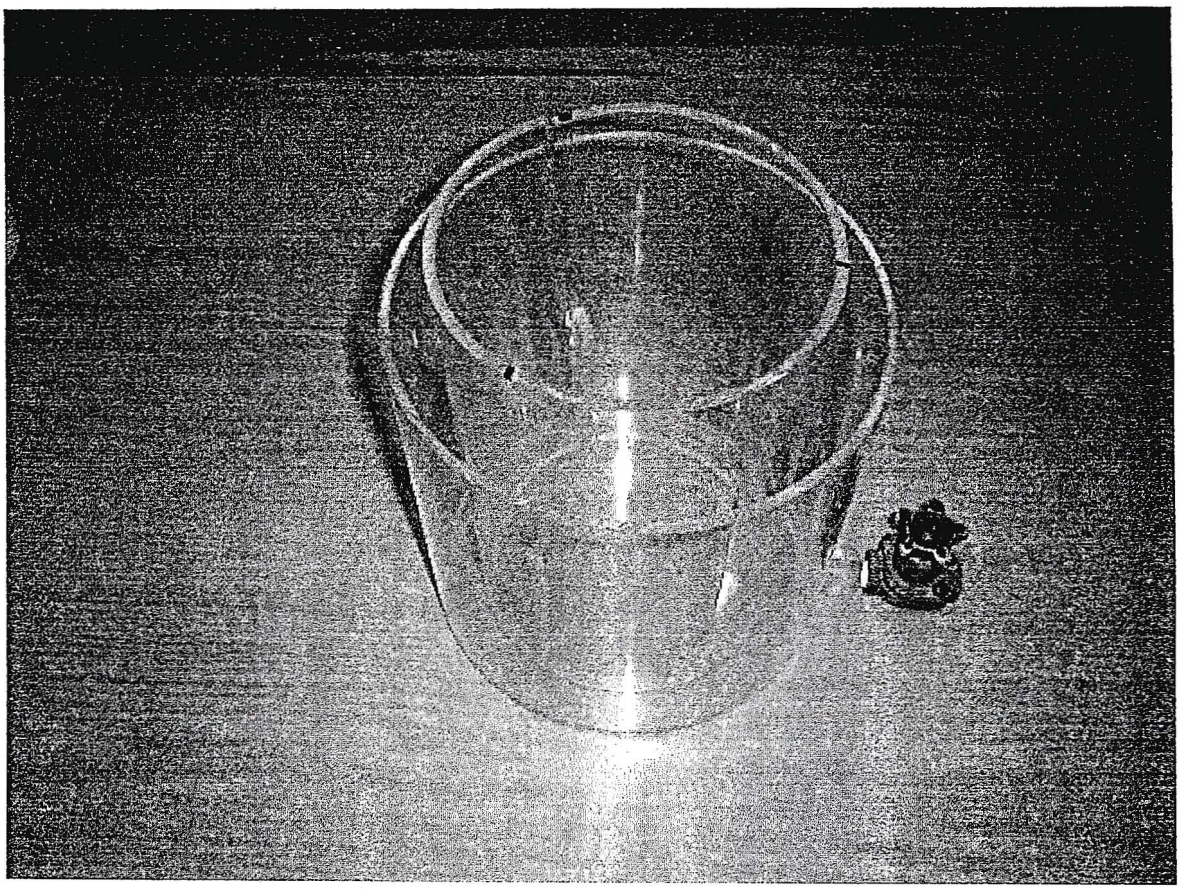


Figure 3.5: Perspex tank

After initial experimentation with the two above-mentioned laboratory tanks, a new tank was made with dimensions exactly one-tenth to that of the plant tank. Further experiments were conducted in this tank.

3.2.2 The Silverson mixer

The mixer that was available at Mondi's laboratory for the agitation of the emulsion was a Silverson mixer, model L2R. This was an old mixer and at times was not able to supply a constant agitation speed to the emulsion. As the emulsion thickened, during the emulsification process, a small decrease in agitation speed was noticed. However the use of this mixer was continued for a few more experiments since the capsule produced were similar in size to the ones produced at the plant and funds were not available to purchase another mixer. The Silverson mixer is shown in Figure 3.3.

The impeller attached to the Silverson mixer was a standard impeller, purchased with the mixer. The impeller, 45 mm in diameter and 11 mm thick, is shown in Figure 3.4.

3.2.3 The laboratory heater and agitator

The laboratory heater was used to heat the colourformer ink to about 105 °C. The agitator was used to ensure homogeneity of the ink and that the dye granules were thoroughly dissolved in the solvent. The heater and agitator are shown in Figure 3.6.

3.2.4 The Malvern Mastersizer

The Malvern Mastersizer (Malvern Instruments Ltd., UK) is an analyser used to measure the microcapsule sizes and its size distribution.

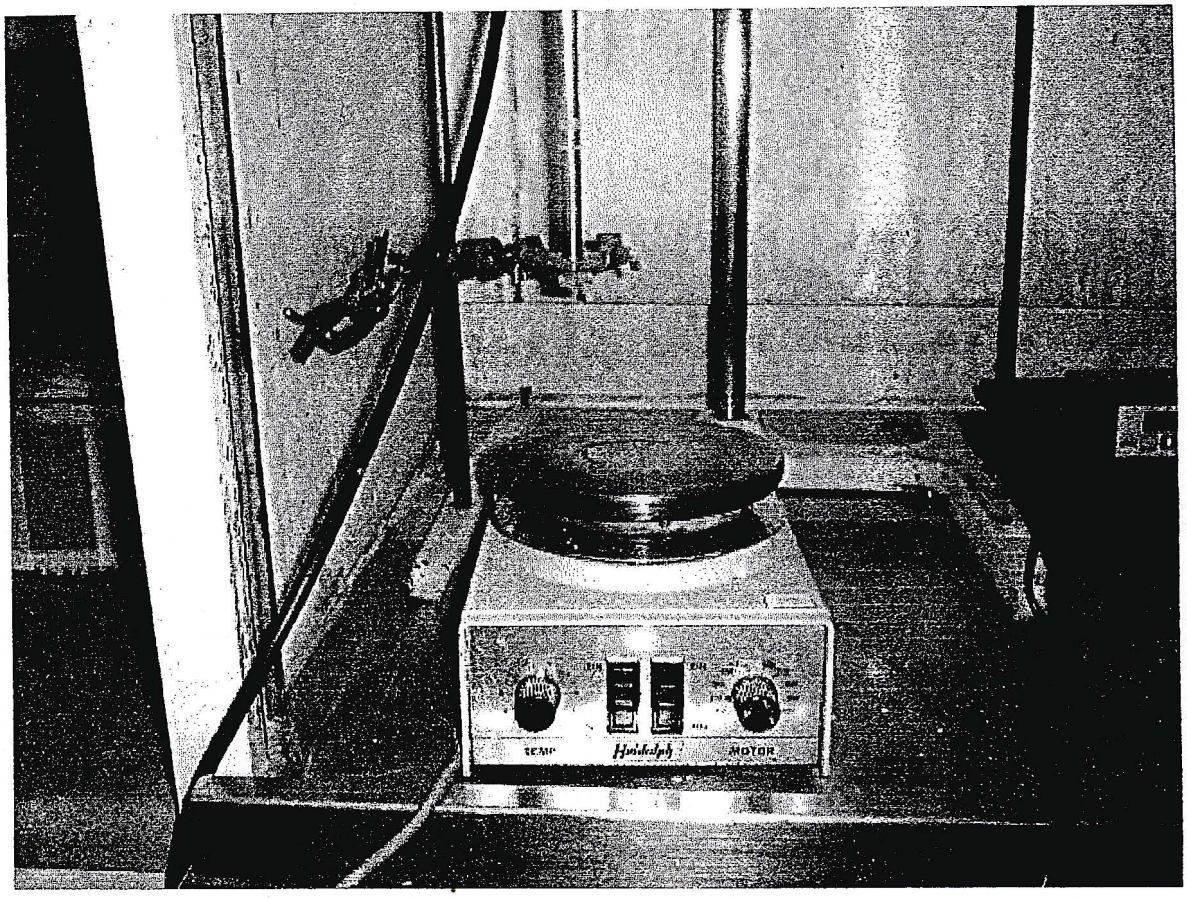


Figure 3.6: Laboratory heater and agitator used for the colourformer oil

The Mastersizer and the computer, which is integrated with the Malvern software, are shown in Figure 3.7. The purpose of the optical unit in the machine is to collect the information from the scattered light when a laser is passed through the sample to be measured. It is the Malvern software that analyses the raw data from the optical unit to calculate the size distribution.

The Mondi Mastersizer has an internal sampling unit, which mixes the sample of microcapsule emulsion to be analysed, with water. The mixture is then pumped to a measurement unit where it is passed through a measurement cell. The water is poured into a 500 ml beaker and drops of the capsule sample are added to it. This ensures that the sample is dilute enough to be passed through the Mastersizer. The beaker is placed under a pump arm, which is then lowered into the sample.

The pump arm consists of a pump, stirrer and an ultrasonic probe that can be used to help disperse the sample.

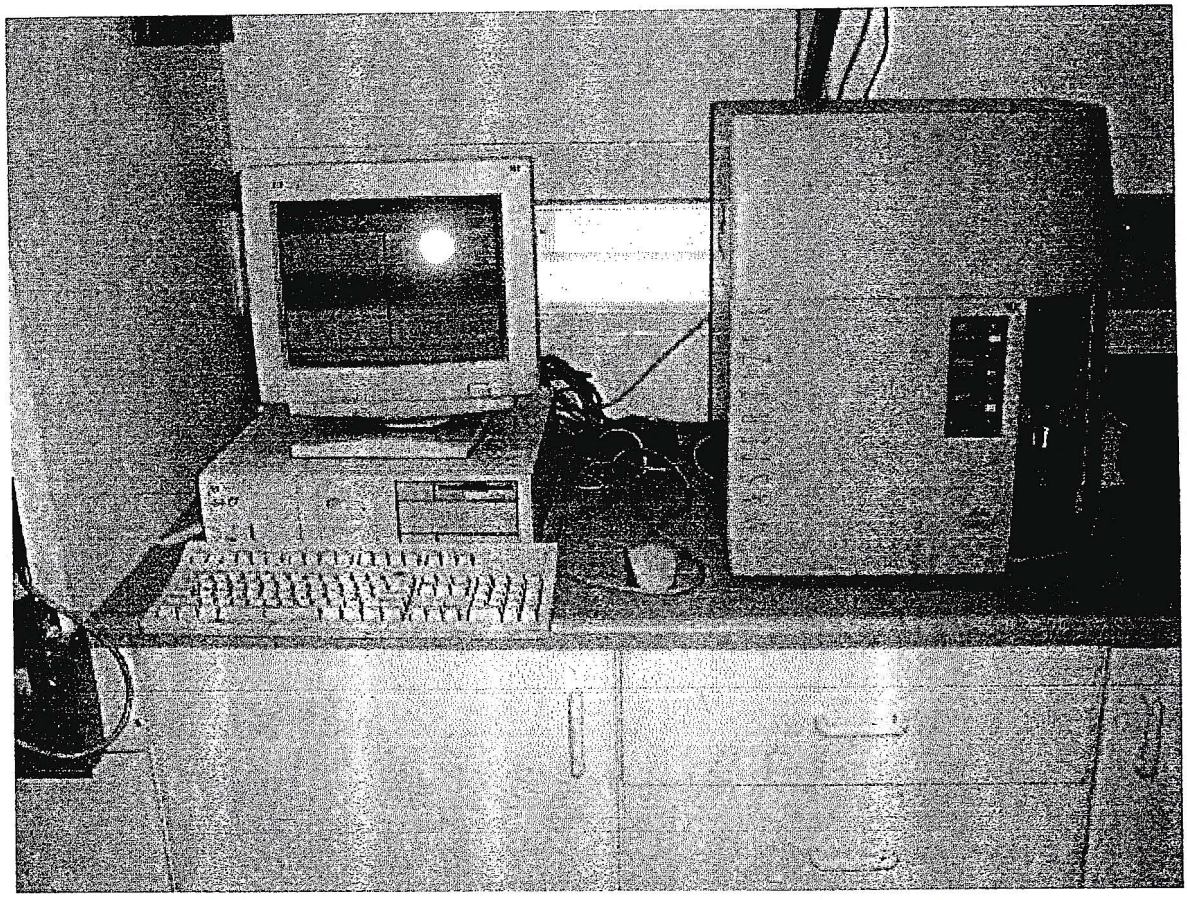
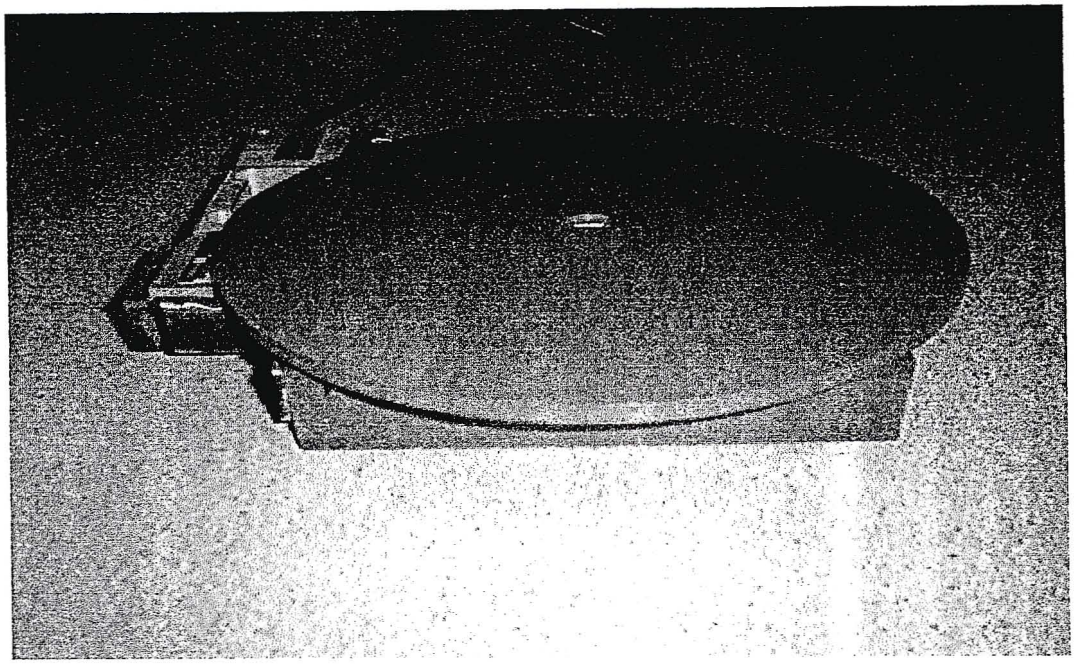


Figure 3.7: Malvern Mastersizer with the computer, for the output of results

3.2.5 Power measurement

The power imparted by the impeller was determined by measuring torque. A turntable, made from hard plastic, was constructed by the chemical engineering workshop, at the University of Natal. It consisted of a flat plate mounted on a square stand by a bearing, which allowed it to rotate, relatively free of friction. A picture of the turntable can be seen in Figures 3.8a and b. The laboratory emulsification tank was placed on top of the turntable. A string was attached from the turntable at an angle of 90° to the arm of a load cell, shown in Figure 3.9.



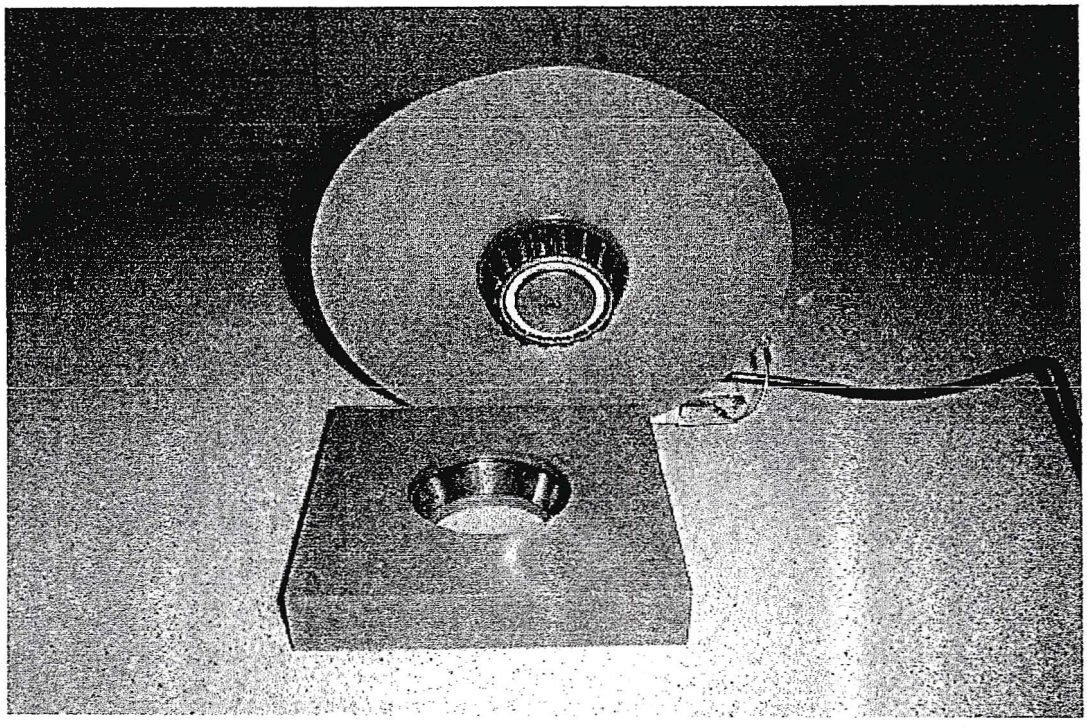


Figure 3.8a, b: Picture of turntable together and separated

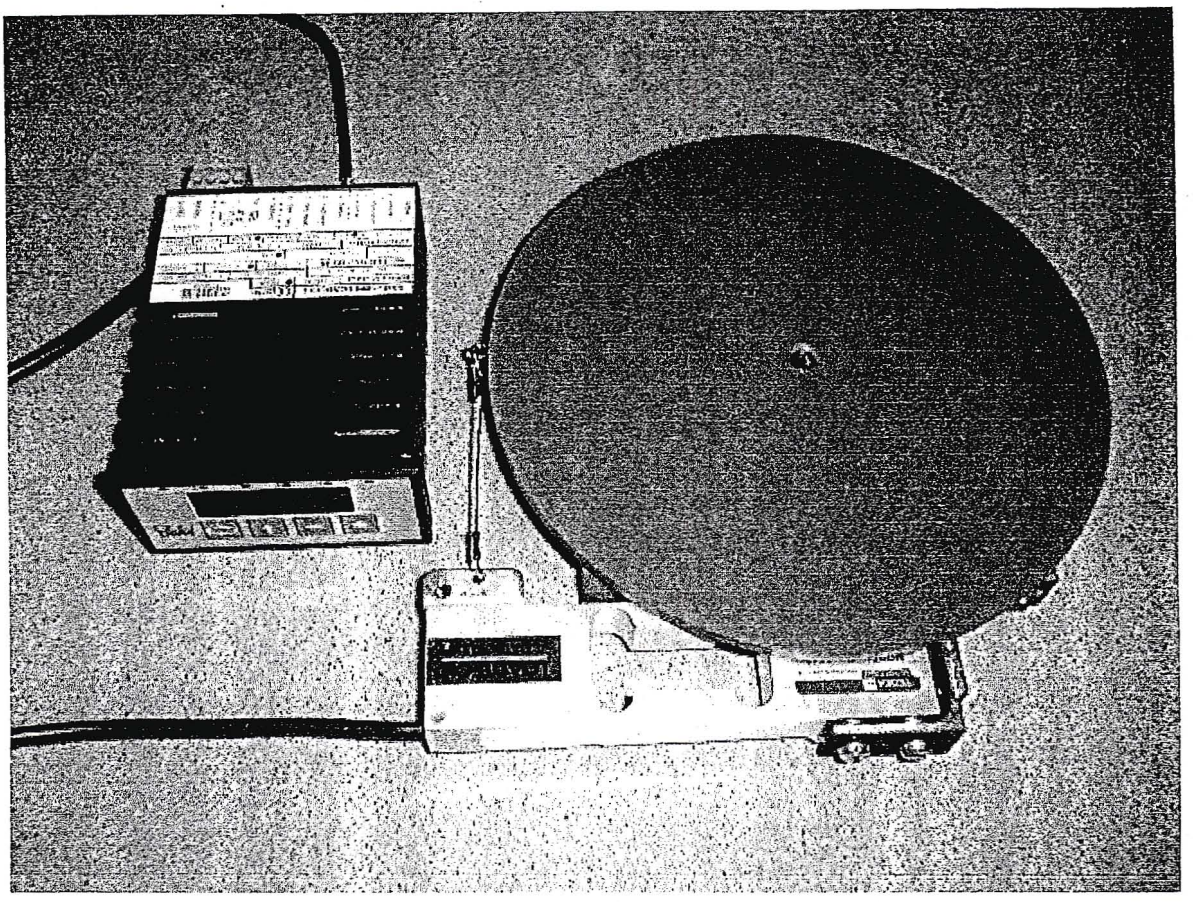


Figure 3.9: Load cell and digital display connected to the turntable

The load cell was connected to a digital display, which served as an indicator. It displayed the forced applied by the string, connected to the arm of the load cell. The force was induced by the rotation of the tank on the turntable, when the impeller was used to agitate the emulsion. A picture of the entire torque setup can be seen in Figure 3.10.

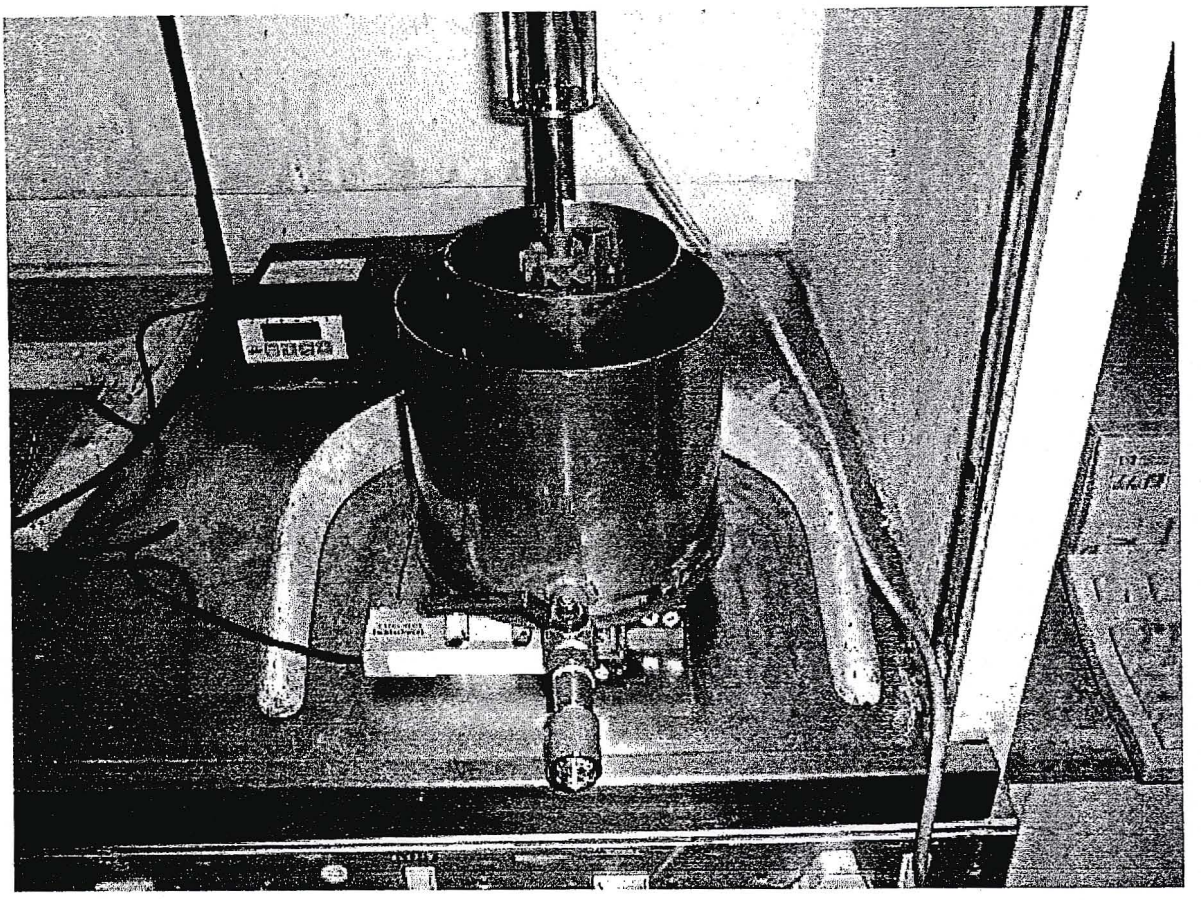


Figure 3.10: Setup of the laboratory equipment for power measurements

3.3 The plant emulsifier

The plant emulsifier is a 3000-liter cylindrical mixing vessel and is constructed from stainless steel. It measures 1.38 m in diameter, 2.00 m high and the emulsion in the tank reaches a height of approximately 1.60 m. The vessel is equipped with three equally spaced baffles, triangular in shape, with dimensions as shown in Figure 3.11. A picture of the vessel can be viewed in Figure 3.12. The impeller is powered by a 45 kW, variable speed motor, and has the ability to drive the impeller at a maximum speed of 1475 rpm. The impeller is a very high shear, flat impeller, of saw-tooth design and measures 0.54 m in diameter. Figure 3.13 shows a picture of the plant impeller used.

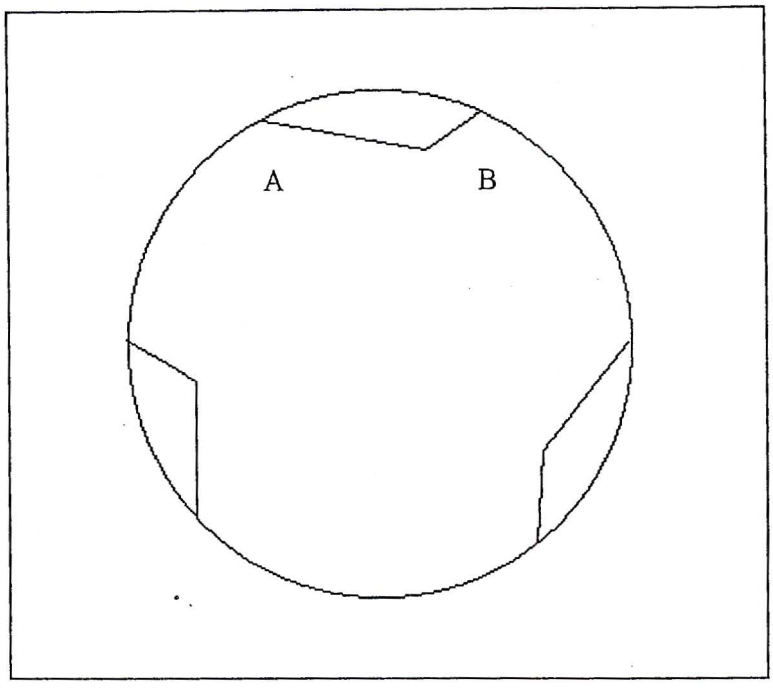


Figure 3.11: Top view of plant emulsifier showing baffle dimensions: Side A = 20 cm and B = 15 cm.

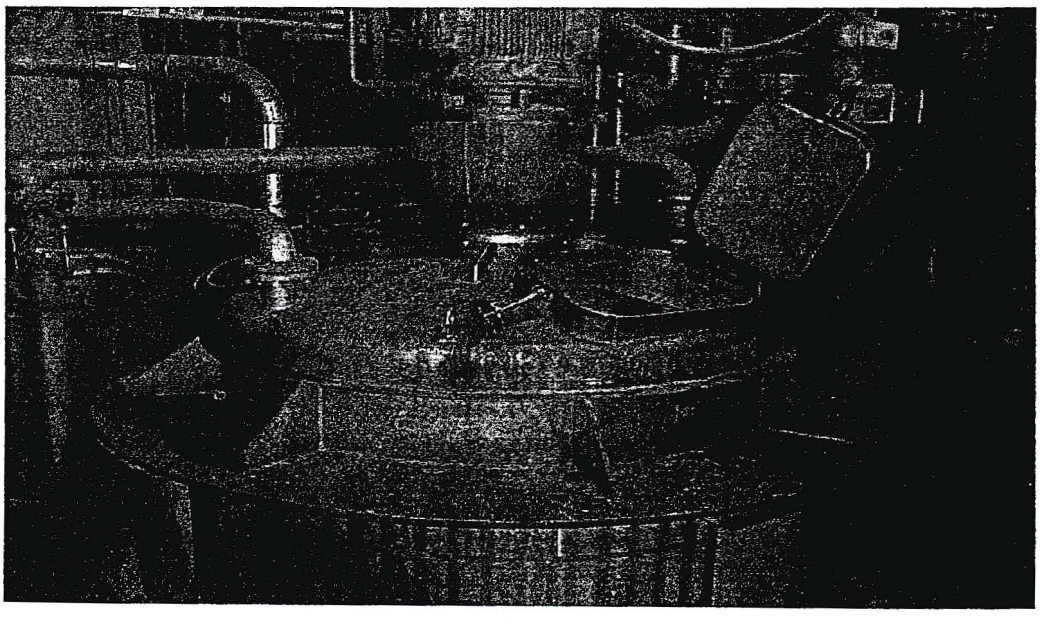


Figure 3.12: The plant emulsifier

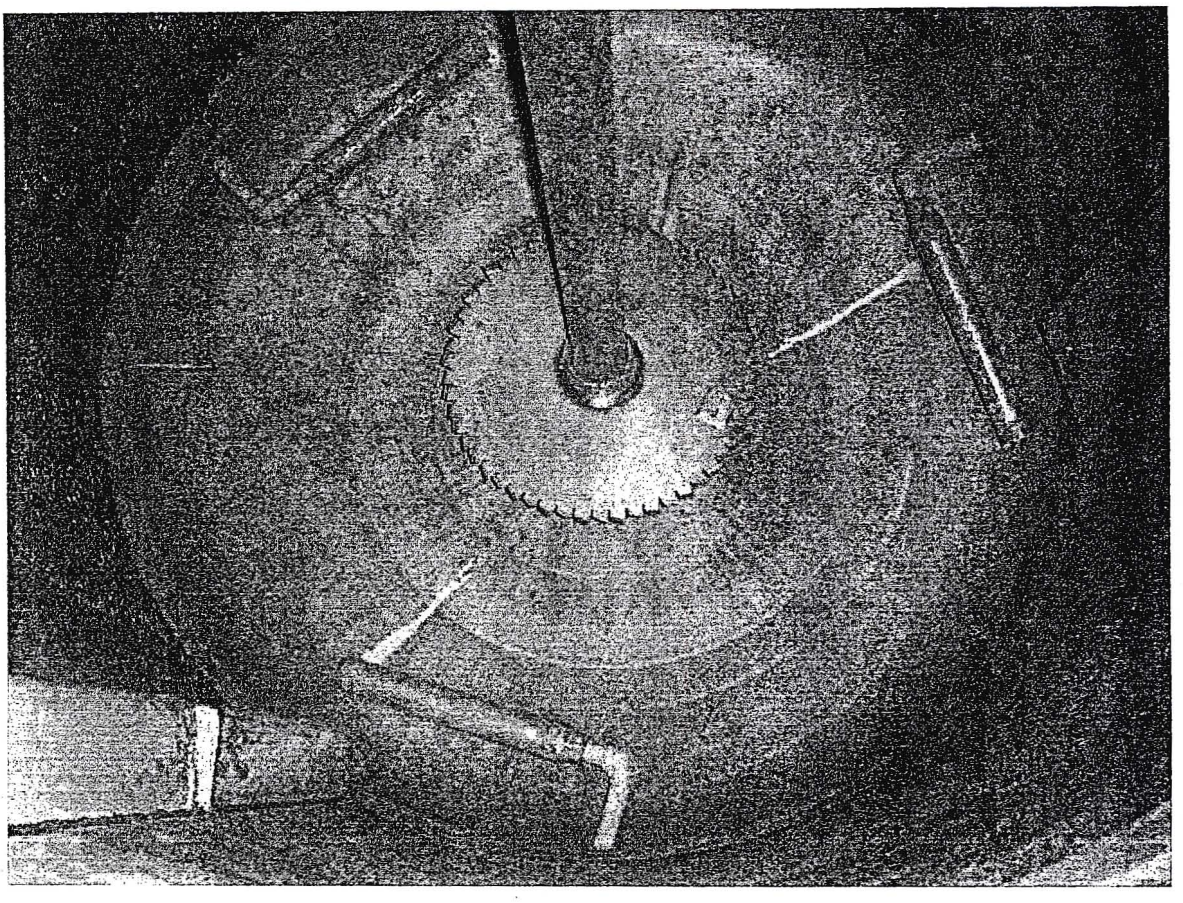


Figure 3.13: Inside of plant emulsifier showing impeller used and baffles

CHAPTER 4

RESULTS AND DISCUSSION

Although the experiments were conducted at the laboratory unit for an emulsification period of 60 minutes, more attention was given to the data that was obtained after 40 minutes, since the emulsification period at the plant is a minimum of 40 minutes. The capsules produced at the plant have the following properties:

- Capsule diameter: 4 – 5 microns - an ideal result.
- Percent undersize capsules (under 2 microns): 25 – 30 per cent - should be much lower than 20 per cent.
- Percent oversize capsules (above 10 microns): 0 – 1 per cent - an ideal result and currently not a problem to Mondi.

4.1 Particle size analysis

Initially there was some concern as to whether the equipment used for the particle size analysis, the Mastersizer, was giving the correct result. The machine had been calibrated and serviced recently, and according to the technicians at the Mondi laboratory, it was performing well. It was decided to produce a batch of capsules on the plant, analyse it at Mondi and then send it to different companies for particle size analysis. The average particle diameter, D, the undersize fractions, U and the oversize fractions, O, obtained from the investigation are shown in Table 4.1. All the companies used a Malvern Mastersizer for the analysis, with the exception of Ciba, who measured the capsules using a Coulter Counter. Mintek also used a Sympatech machine in addition to a Mastersizer. The sample of microcapsules was sent to Ciba at a later stage. A different, but similar sample was sent.

microns, undersize of 31.75% and oversize of 0%. The results from Ciba are therefore shown together with the results obtained from the rest of the companies below.

Table 4.1: Particle size analysis from different companies

Companies	D (microns)	U (%)	O (%)
Mondi	4.03	29.23	0.04
BASF	5.50	2.60	0.10
Micron Scientific	3.55	22.00	x
Ciba - Coulter	4.16	15.21	x
Mintek - Malvern	4.56	27.00	3.00
Mintek - Sympatech	4.19	29.00	2.00

From the printouts of the results obtained from Micron Scientific and Ciba, it was not possible to determine the fraction of oversize capsules produced, represented by 'x'. However, it should be noted that the amount of oversize capsules produced at Mondi is not considered to be a problem.

All the companies have mentioned that the analysis was repeated several times and an average was sent to Mondi. BASF in Germany have measured the capsules from the plant at Mondi to be almost perfect. The difference in the percentage undersize was alarming. The undersize fraction of capsules was 2.60%, which is what Mondi desire. Previous analyses from BASF have given similar results, which is different from that at Mondi. BASF insists that the capsules produced at Mondi were the best they have seen, but this was not the case when the capsules were analysed in the Mondi laboratory.

Ciba also measured a lower percentage of undersize capsules, 15.21%. This is probably due to the different equipment used for the analysis. Ciba also recommends that the capsules produced at Mondi should have an average diameter of about 7 microns. If this were implemented, the

percentage of undersize capsules would drop to about 15%. However, 7 micron-sized capsules are too large and Mondi would experience problems when the capsules are being coated on paper.

BASF has recently sent details of their "mode of presentation" to Mondi. The presentation mode refers to the manner in which the Mastersizer interprets the data, when a microcapsule sample is passed through it. The result of changing the presentation mode on Mondi's Mastersizer, to that of BASF's was surprising. Figures 4.1 and 4.2 shows the size distribution curves obtained using the old and new presentation modes. The differences to the old presentation mode that was noticed were:

- A unimodal curve was now being produced, instead of the previous bimodal curve.
- The amount of undersize capsules produced was now less than 2%.
- The capsule diameter showed an increase of about 0.5 microns.

The above changes were noticed with all the experiments conducted, including the batches made at the chemical plant. This proves that BASF does indeed measure the capsules differently. Microcapsule emulsions were then viewed under a microscope in order to decide which interpretation of the results was correct. The results presented here are all consistent with Mondi's interpretation.

4.2 Microscopic evaluation of the emulsion

Several microcapsule emulsions were produced, together with the hardening step, in the laboratory at Mondi. Two sets of samples were produced using Mondi's and BASF's presentation modes. Samples of each emulsion were viewed under a light microscope and the average results are tabulated below. The microscopy was done in order to determine whether the Malvern Mastersizer produced worthy analyses.

Result: Analysis Report

Sample Details

Sample ID: RUN 3B - T=30
Sample File: TEST1
Sample Path: C:\SIZERMU\DATA\
Sample Notes: NEW SCALE-DOWN TANK
7500 RPM...20 MIN
7200 RPM...20 MIN
SAMPLE 3 - 30 MIN AFTER ACID ADDITION

Run Number: 3
Record Number: 1101

Measured: 10 Jan 2002 11:38
Analysed: 10 Jan 2002 11:38
Result Source: Analysed

System Details

Sampler: B
Presentation: 4OHD
Analysis Model: Polydisperse
Modifications: None

[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Measured Beam Obscuration: 22.3 %
Residual: 0.536 %

Result Statistics

Distribution Type: Volume
Mean Diameters:
D [4, 3] = 4.95 um

Concentration = 0.0098 %Vol
D (v, 0.1) = 0.67 um
D [3, 2] = 2.13 um

Density = 1.000 g / cub. cm
D (v, 0.5) = 5.19 um
Span = 1.487E+00

Specific S.A. = 2.8153 sq. m / g
D (v, 0.9) = 8.38 um
Uniformity = 4.266E-01

Size Low (um)	In %	Size High (um)	Under%	Size Low (um)	In %	Size High (um)	Under%
0.31	0.82	0.36	0.82	10.48	1.82	12.21	99.52
0.36	1.57	0.42	2.38	12.21	0.48	14.22	100.00
0.42	2.19	0.49	4.57	14.22	0.00	16.57	100.00
0.49	2.62	0.58	7.19	16.57	0.00	19.31	100.00
0.58	2.84	0.67	10.03	19.31	0.00	22.49	100.00
0.67	2.83	0.78	12.86	22.49	0.00	26.20	100.00
0.78	2.59	0.91	15.45	26.20	0.00	30.53	100.00
0.91	2.15	1.06	17.60	30.53	0.00	35.56	100.00
1.06	1.58	1.24	19.18	35.56	0.00	41.43	100.00
1.24	0.97	1.44	20.14	41.43	0.00	48.27	100.00
1.44	0.46	1.68	20.60	48.27	0.00	56.23	100.00
1.68	0.09	1.95	20.69	56.23	0.00	65.51	100.00
1.95	0.26	2.28	20.95	65.51	0.00	76.32	100.00
2.28	0.81	2.65	21.76	76.32	0.00	88.91	100.00
2.65	1.92	3.09	23.68	88.91	0.00	103.58	100.00
3.09	3.86	3.60	27.53	103.58	0.00	120.67	100.00
3.60	6.77	4.19	34.31	120.67	0.00	140.58	100.00
4.19	10.51	4.88	44.82	140.58	0.00	163.77	100.00
4.88	13.73	5.69	58.55	163.77	0.00	190.80	100.00
5.69	14.58	6.63	73.13	190.80	0.00	222.28	100.00
6.63	12.15	7.72	85.28	222.28	0.00	258.95	100.00
7.72	8.08	9.00	93.35	258.95	0.00	301.68	100.00
9.00	4.35	10.48	97.70				

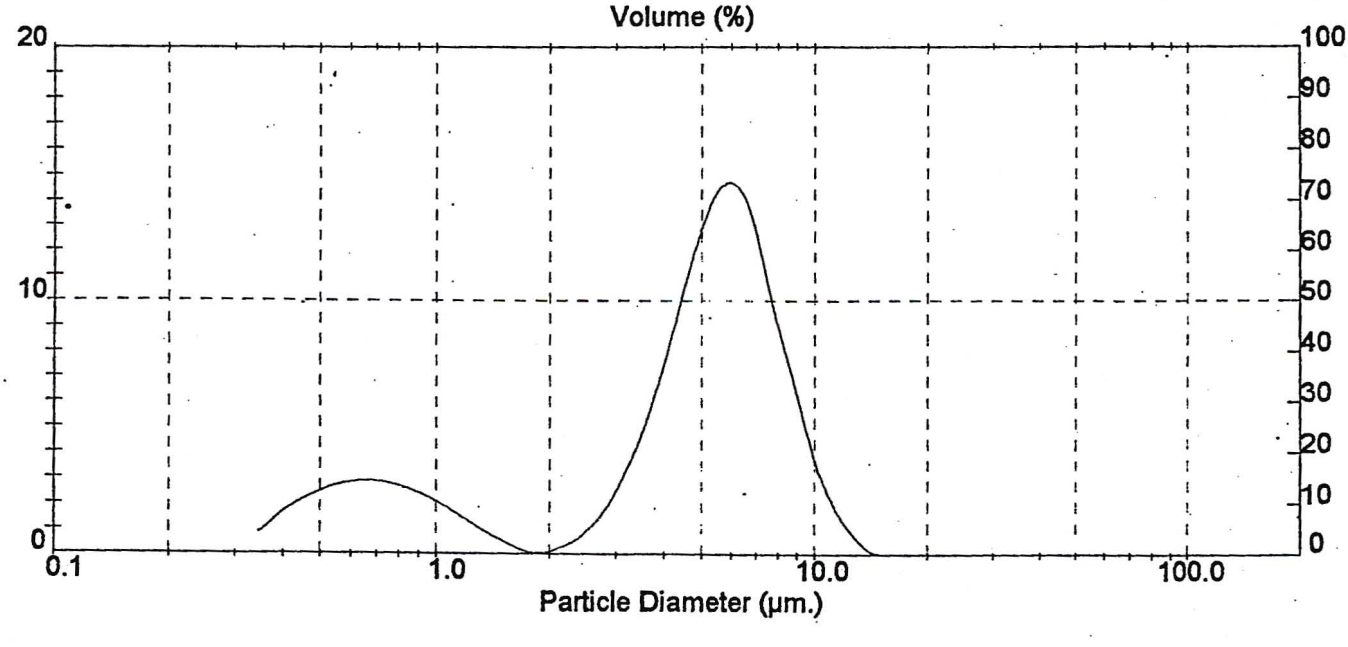


Figure 4.1: Size distribution using Mondi's presentation mode

Result: Analysis Report

Sample Details

Sample ID: RUN 3B - T=30
Sample File: (Result Not Saved)
Sample Path: C:\SIZERMU\DATA\
Sample Notes: NEW SCALE-DOWN TANK
7500 RPM...20 MIN
7200 RPM...20 MIN
SAMPLE 3 - 30 MIN AFTER ACID ADDITION

Run Number: 8

Measured: 10 Jan 2002 11:38
Analysed: 10 Jan 2002 11:55
Result Source: Analysed

System Details

Sampler: B
Presentation: 4OAD
Analysis Model: Polydisperse
Modifications: None

[Particle R.I. = (1.5295, 0.0000); Dispersant R.I. = 1.3300]

Measured Beam Obscuration: 22.3 %
Residual: 0.622 %

Result Statistics

Distribution Type: Volume
Mean Diameters:
D [4, 3] = 6.01 um

Concentration = 0.0168 %Vol
D (v, 0.1) = 3.53 um
D [3, 2] = 5.29 um

Density = 1.000 g / cub. cm
D (v, 0.5) = 5.70 um
Span = 9.408E-01

Specific S.A. = 1.1346 sq. m / g
D (v, 0.9) = 8.89 um
Uniformity = 3.001E-01

Size Low (um)	In %	Size High (um)	Under%	Size Low (um)	In %	Size High (um)	Under%
0.31	0.00	0.36	0.00	10.48	2.94	12.21	98.92
0.36	0.00	0.42	0.00	12.21	0.94	14.22	99.86
0.42	0.00	0.49	0.00	14.22	0.14	16.57	100.00
0.49	0.00	0.58	0.00	16.57	0.00	19.31	100.00
0.58	0.00	0.67	0.00	19.31	0.00	22.49	100.00
0.67	0.00	0.78	0.00	22.49	0.00	26.20	100.00
0.78	0.00	0.91	0.00	26.20	0.00	30.53	100.00
0.91	0.00	1.06	0.00	30.53	0.00	35.56	100.00
1.06	0.00	1.24	0.00	35.56	0.00	41.43	100.00
1.24	0.00	1.44	0.00	41.43	0.00	48.27	100.00
1.44	0.00	1.68	0.00	48.27	0.00	56.23	100.00
1.68	0.01	1.95	0.01	56.23	0.00	65.51	100.00
1.95	0.40	2.28	0.41	65.51	0.00	76.32	100.00
2.28	1.32	2.65	1.73	76.32	0.00	88.91	100.00
2.65	2.93	3.09	4.66	88.91	0.00	103.58	100.00
3.09	6.38	3.60	11.04	103.58	0.00	120.67	100.00
3.60	10.60	4.19	21.64	120.67	0.00	140.58	100.00
4.19	12.40	4.88	34.04	140.58	0.00	163.77	100.00
4.88	15.84	5.69	49.88	163.77	0.00	190.80	100.00
5.69	17.03	6.63	66.91	190.80	0.00	222.28	100.00
6.63	12.79	7.72	79.70	222.28	0.00	258.95	100.00
7.72	11.01	9.00	90.71	258.95	0.00	301.68	100.00
9.00	5.27	10.48	95.98				

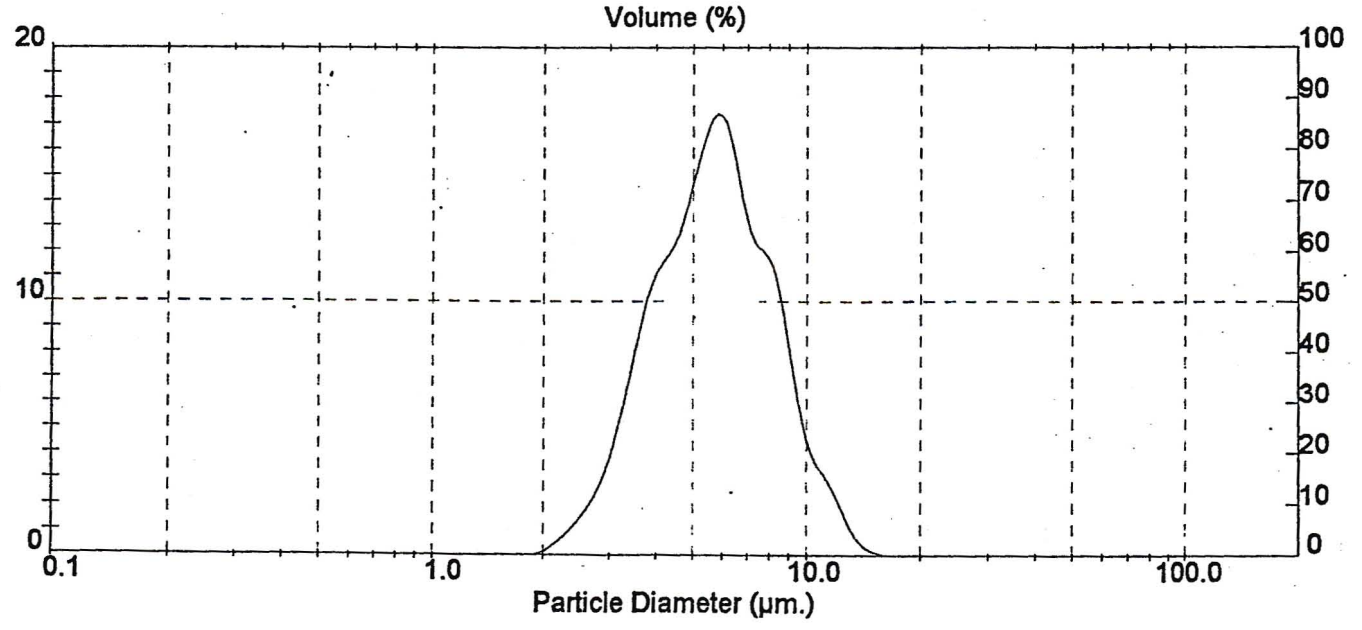


Figure 4.2: Size distribution using BASF's presentation mode

Table 4.2: Average results showing Mondi and BASF presentation mode

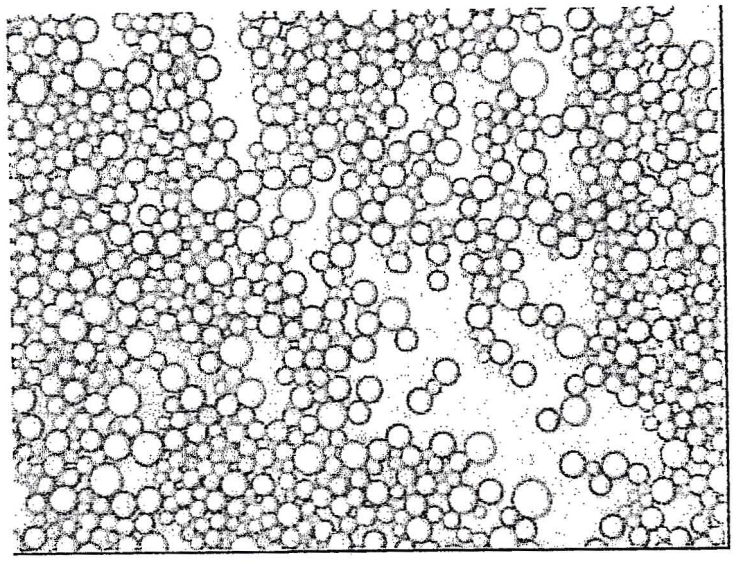
	Mondi (4OHD)	BASF (4OAD)	Microscope
D (m)	3.53	4.26	5.05
U (%)	32.77	12.53	2

The capsules viewed under the microscope were photographed and evaluated by counting the number of capsules in each size range, from 0 to 10 microns. This was done for ten different slides. Two examples of the pictures of the capsules are shown in Figures 4.3a and b. The volume of capsules is proportional to Nd^3, where N is the number of capsules and d is the diameter of the capsules in a particular size range. Hence the volume percent of the capsules was calculated using:

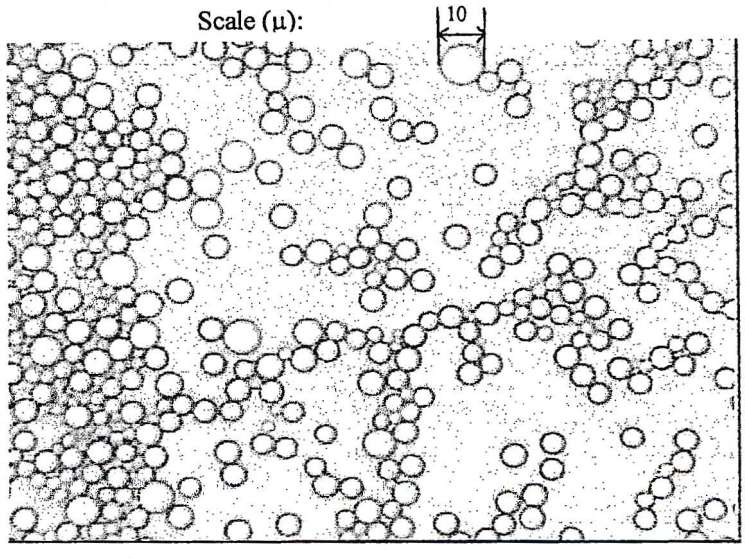
$$V(\%) = Nd^3 / \Sigma Nd^3 \qquad (4.1)$$

A general curve of the results is plotted in Figure 4.4. The Mondi and BASF results shown on Table 4.2 were obtained directly from the Mastersizer graphs, which are plotted on a log scale. This representation magnifies the importance of the first peak (tiny capsules) shown on the graph. When these graphs were re-normalised for representation on a linear scale, using Equation 4.1, Figure 4.5 was obtained. These graphs show that the volume fraction of undersized capsules may be small or even insignificant.

Note: The samples used for comparison of size distribution methods were produced in the laboratory emulsifier, using a higher than normal impeller speed throughout (8000 rpm), to ensure well-controlled conditions and a significant proportion of undersize (Pages 57 and 58 show a reduction in speed). Size distribution data from tests at 'normal' speed (7500 rpm) are shown in Appendix C.



(a)



(b)

Figures 4.3 a, b: Examples of the pictures of the microcapsules viewed under a microscope

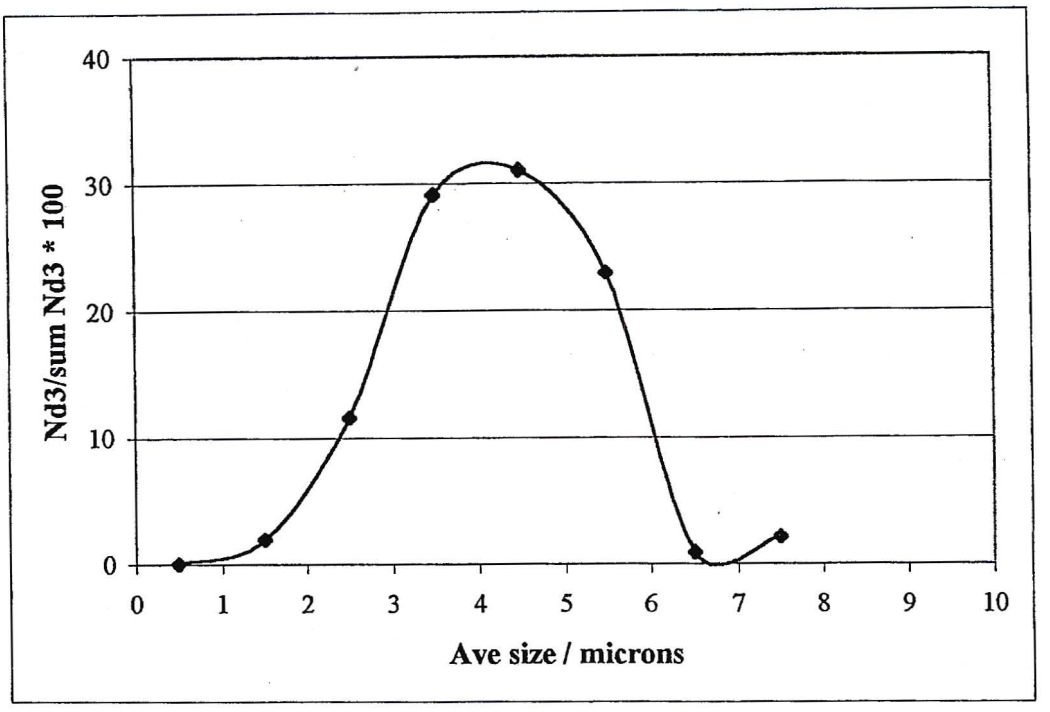


Figure 4.4: Volume distribution based on microscopy

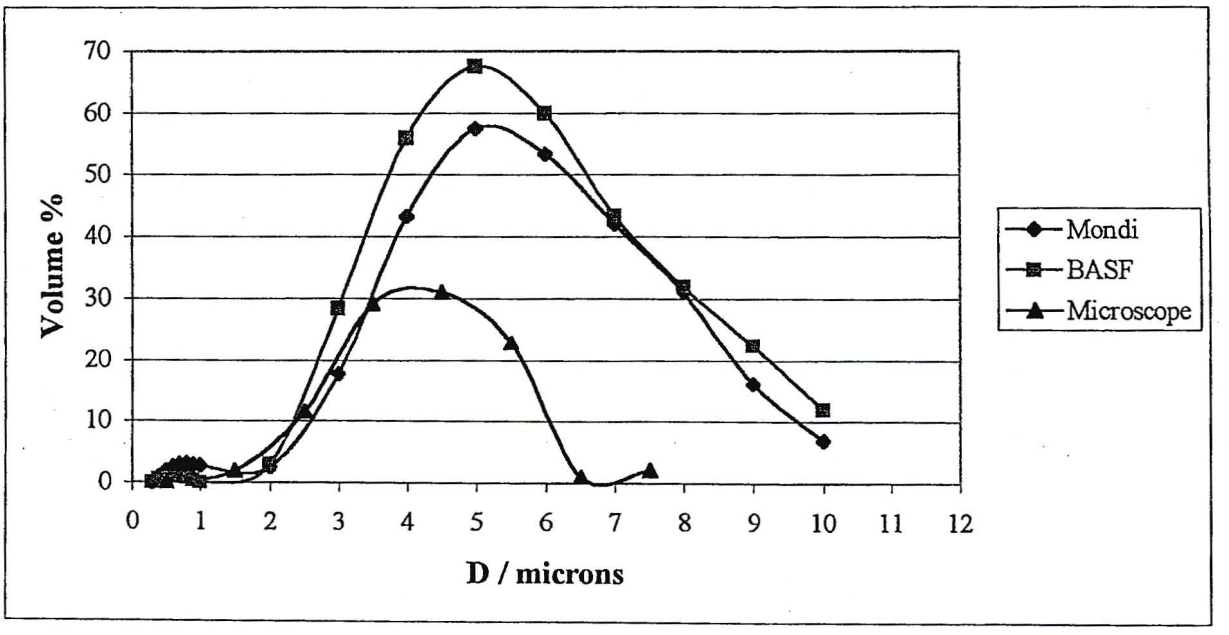


Figure 4.5: Mastersizer curves, which have been re-normalized using delta D of unity

4.3 Experimental results

The main aim was to reduce the percentage of undersize capsules, without affecting any other properties. However before the results can be analysed and discussed, there should be an understanding of how the Mastersizer actually measures the particle sizes, and calculates the results. A brief explanation on how the Mastersizer works is given, according to The Mastersizer Manuals [1995].

4.3.1 Some fundamental concepts of the Mastersizer

In order to understand the full meaning of the results obtained from the Mastersizer, it should be noted that the size distribution is volume based (i.e. per cent of total volume of particles between given sizes). The microcapsule diameters are expressed in terms of equivalent spheres. The theory, which the Mastersizer uses to calculate the parameters of the microcapsules, is called the Mie theory. This theory presumes that the particles measured are perfect spheres. The Mastersizer first uses the volume of the particle to calculate its size, by calculating the diameter of an imaginary spherical particle, based on the volume. Figure A.1, Appendix A, gives an example of a typical printout from the Mastersizer.

The statistics of the distribution are calculated from the results using the derived diameters D[m,n]. This is an internationally agreed method for defining the mean and other moments of particle size. An explanation is given below of some of the common parameters, which are used to describe the microcapsules. D(v, 0.5), D(v, 0.1) and D(v, 0.9) are standard "percentile" readings from the analysis.

- D(v, 0.5) is the size of the particle at which 50% of the particle is smaller and 50% is larger than this size. This value is also known as the Mass Median Diameter (MMD).
- D(v, 0.1) is the size of the particle for which 10% of the sample is below this size.
- D(v, 0.9) gives the size of particle for which 90% of the sample is below this size.
- D[4,3] is the volume mean diameter.

- D[3,2] is the surface area mean diameter. It is also known as the Sauter mean.
- The "obscuration" helps the user to set the concentration of the sample when it is added to the dispersant, before it goes into the Mastersizer. It is the measure of the amount of laser light lost due to the introduction of the sample within the analyser beam. For the microcapsule emulsion, an ideal range is between 20 and 25%.

4.3.2 Agitation speed variation

The plant agitator runs at an optimum speed of 75% during the bulk of the emulsification period. This translates into approximately 775 rpm, from Figure B1, Appendix B, which was supplied by Mondi. In order to simulate this speed using the laboratory equipment, several tests were done to try and obtain the desired capsule size, by manipulating the impeller speed. Not only should the mean capsule diameter be within the desired range, but also the spread of sizes, e.g. the percent undersize. Figures 4.6 to 4.8 shows the results obtained from these experiments. The speed settings on the Silverson mixer were irregular since it is an old model and there are no pre-set speeds. A tachometer was used to mark off speeds at different levels, i.e. 8000, 7500, 7200, 6600, 6100, 5540, 5000, and 3270 rpm.

From Figure 4.7 it was noticed that a decrease in the impeller speed resulted in a desirable decrease in the percentage of undersize capsules. The lowest speed used, 6600 rpm, produced 15% of undersize capsules after 40 minutes of agitation. At 7200 rpm, 20% of undersize capsules were observed, which was also a very good result. For these two speeds however, the mean capsule diameter increased beyond the specified range to approximately 7.16 and 7.57 microns respectively, which can be seen in Figure 4.6. The percentage of oversize capsules was also increased, to above 3%, as the impeller speed decreased. At an impeller speed of 8000 rpm, an average capsule diameter of 1.93 microns and 67.02% of undersize capsules were observed. This occurred due to the very high shearing action that resulted from the high impeller speed. No oversize particles were observed. The speed at which the desired capsule size as well as an accepted percentage of undersize and oversize capsules was reached, was 7500 rpm. At this speed, an average capsule diameter of 5.12 microns and 24.20% of undersize capsules were observed. The percentage of oversize capsules was 1.63%. Since these results were more or less similar to the results obtained at the plant, 7500 rpm was used as a "standard" speed to conduct the rest of the experimental work.

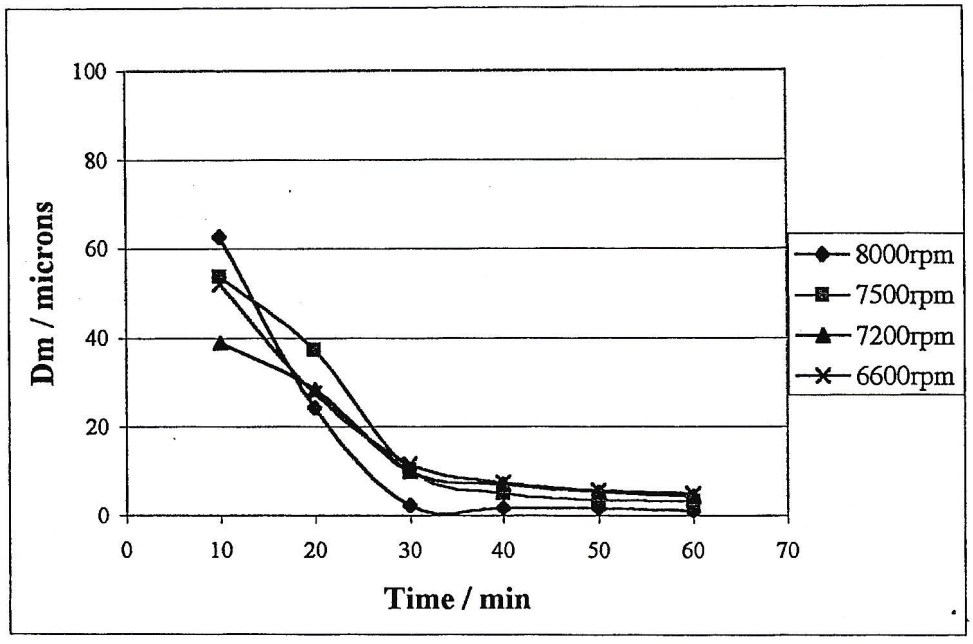


Figure 4.6: Speed variation showing the average capsule diameter

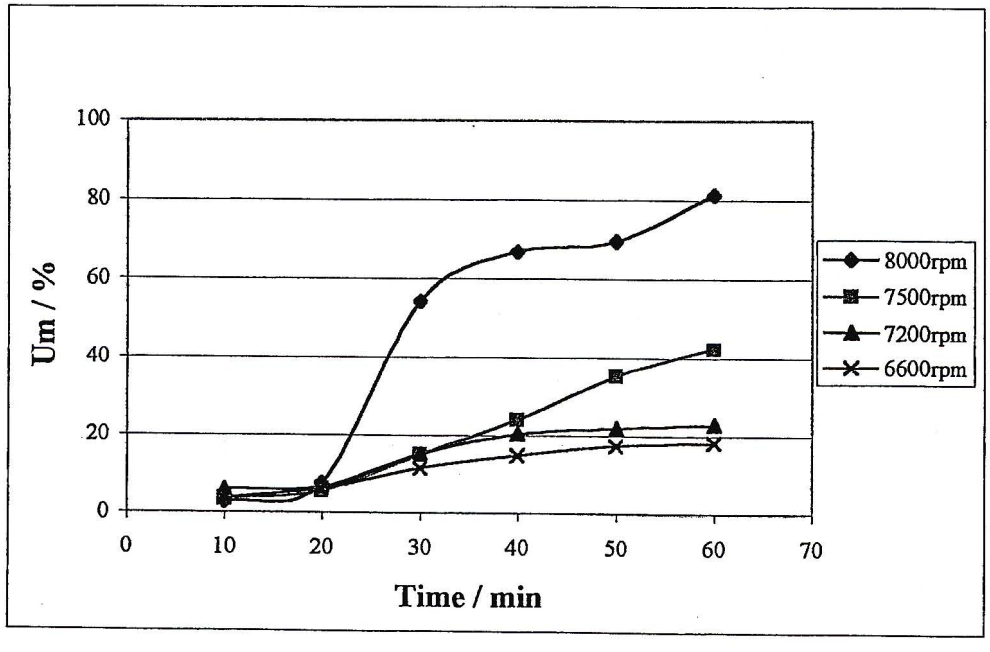


Figure 4.7: Speed variation showing the average undersize particles

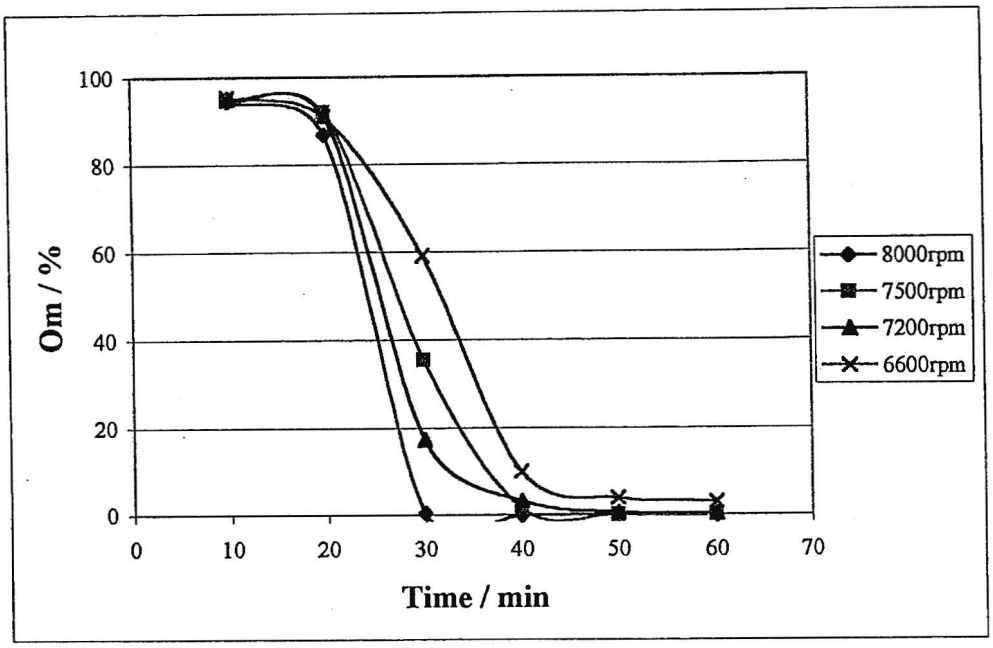


Figure 4.8: Speed variation showing the average oversize particles

4.3.3 Temperature variation

The literature survey revealed that there was a significant difference in the preferred emulsification temperature for various patented processes for microcapsule production. Sanchez et al [1998] described a bimodal droplet size distribution (DSD) curves with increasing temperatures. Since it has been stated that the process is very sensitive to temperature changes, an investigation was carried out to determine how temperature affects the capsule size, and its distribution. The temperatures used for experimentation ranged from 22 to 40 °C, in increments of 2 °C. Initially it was decided to vary the temperature from 20 to 40 °C. However, the cooling water available was not cold enough to cool the emulsion to 20 °C, and the high impeller speed during the emulsification contributed to the quick rise in temperature. According to the plant operators at Mondi, temperatures higher than 40 °C would lead to an increase in reaction rate and a lower quality of microcapsules. In this case the capsule wall would not completely polymerise over the entire capsule within the specified emulsification time, and more time would be needed.

An emulsification temperature of 30 °C was used for both plant operations and laboratory tests. This temperature was therefore chosen as a "standard" temperature for further work. The agitation speed, at which the temperature variation experiments were conducted at, was 7500 rpm, since this speed was found to be most suitable.

It was noticed, from Figures 4.9 and 4.10, that at temperatures below 30 °C, the desired capsule diameter was not achieved, after a period of 40 minutes but the amount of undersize capsules was well within specifications. This was due to the fact that at low temperatures, the reaction rate is low and more time was required to achieve the desired size. The emulsion was also noticed to be less viscous than normal after 40 minutes and oil was observed in the emulsion. Emulsifying for a longer period of time, than required, would mean a higher operating cost for Mondi, which is unacceptable. The amount of oversize capsules produced at the lower temperatures was more than 2%, which is also unacceptable.

At temperatures higher that 30 °C, the capsule diameter seemed to be acceptable, but slightly larger than the desired size. The amount of undersize capsules produced was also acceptable, with the exception of the experiment done at 40 °C. The amount of undersize capsules produced was 46.51%, after 40 minutes of emulsification. This occurred since the reaction rate increased too high at the high temperature, resulting in oil droplets being completely encapsulated before 40 minutes. These capsules were then exposed to a longer agitation period, since they were encapsulated quicker. The emulsion was also too viscous to be coated on paper. The capsule diameter was also smaller than that at the other temperatures. The amount of oversize capsules produced at the higher temperatures was within specification, less than 1% on average, as seen in Figure 4.11.

Figure 4.10 shows a decrease in the percentage of undersize capsules produced at temperatures below and above 30 °C. The proportions were 17.12%, and 23.87% respectively. An average of 20 experiments were taken for this calculation. Appendix E is an example of the curves obtained, showing the reproducibility of the data. Although the amount of undersize capsules produced decreased, Figure 4.9 shows that the capsule diameter increased beyond the specified range, i.e. an average of 7.77 microns at temperatures below 30 °C, and an average of 5.59 microns at temperatures above 30 °C.

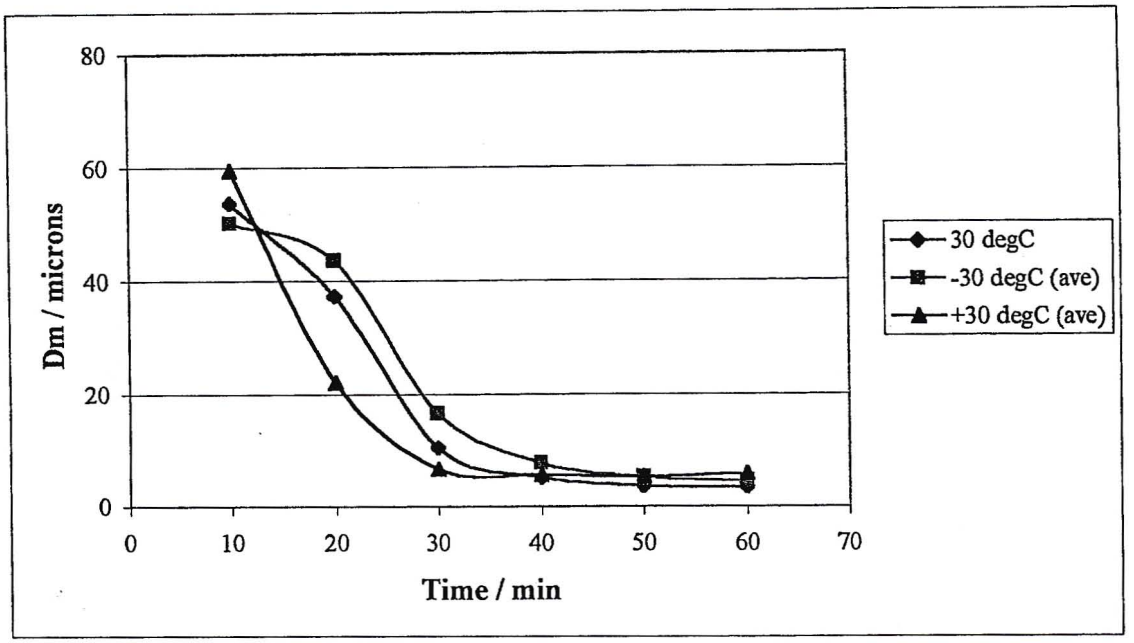


Figure 4.9: Temperature variation showing the average capsule diameter

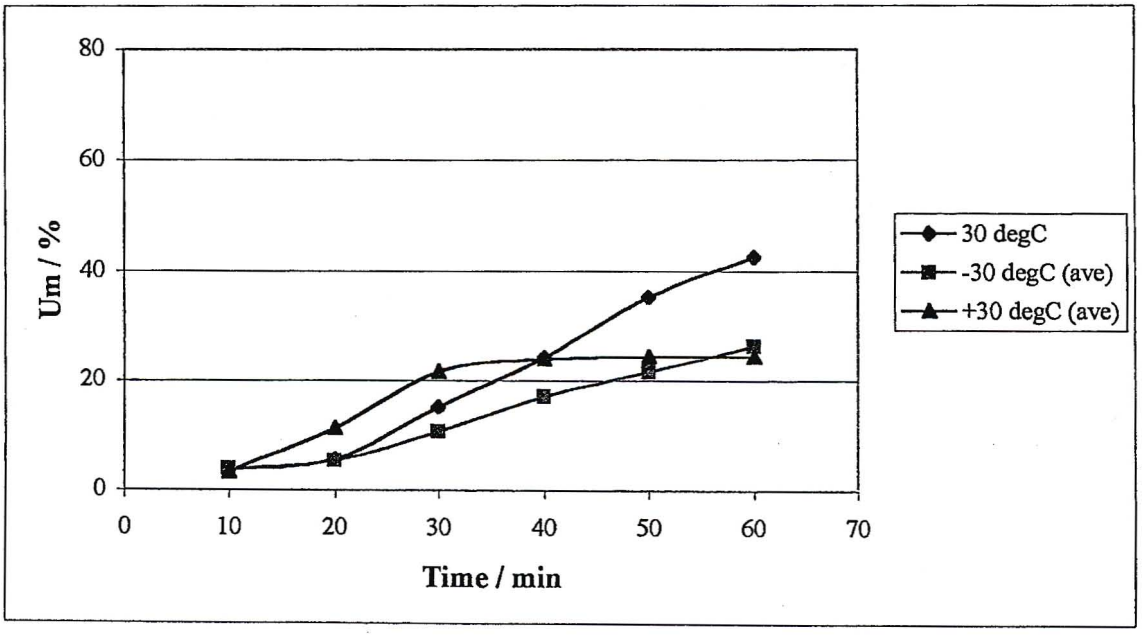


Figure 4.10: Temperature variation showing the average undersize capsules

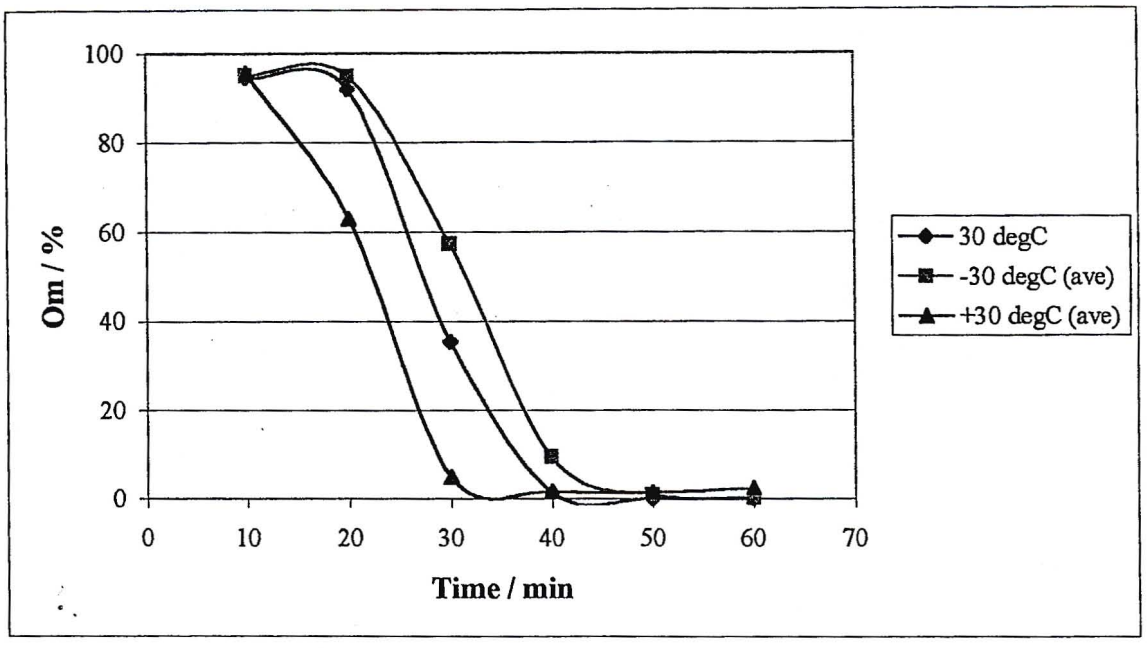


Figure 4.11: Temperature variation showing the average oversize capsules

According to Cao et al. [2000], the particle diameters increased at the higher temperatures because the adsorption rate of the surfactant and the viscosity of the continuous phase were reduced. According to Sanchez et al., high temperatures induce coalescence of the emulsion but also favour the disruption of droplets, leading to bimodal distributions. The above are consistent with the results reported here and also with those observed by Mlynek & Resnick [1972]. The results obtained indicate that the temperature of 30 °C, which is currently being used at the chemical plant at Mondi, is the optimum temperature to run at. A capsule diameter of 5.12 microns, undersize of 24.20% and an oversize of 1.63% were produced at this temperature. These parameters became the benchmark for optimising the other operating variables.

The tests conducted between 22 and 40 °C, produced droplet size distributions, which were always bimodal in the range of the agitation speed studied. When the energy input was increased, by temperature or speed increases, more smaller particles were produced, which is undesirable. When the energy input was decreased, the larger particles were more numerous, which is also undesirable.

4.3.4 Reduction in agitation speed

The size distribution produced at a temperature of 30 °C and an impeller speed of 7500 rpm averaged a diameter of 5.12 microns, 24.20% undersize and 1.63% oversize. These were similar to the size distribution obtained at the plant. In order to reduce the amount of undersize capsules, either the emulsification temperature or the agitation speed had to be varied. The temperature variation runs, done for this study, have proved futile. It was therefore decided to vary the impeller speed by agitating the emulsion at 7500 rpm for the first 20 minutes, and then reducing the speed to 7200 rpm for the remainder of the emulsification period. This would mean that less shear would be applied once the emulsion was formed, hopefully reducing the proportion of undersize capsules. However, a larger average capsule diameter and a larger amount of oversize capsules were expected.

Figures 4.12 to 4.14 shows a comparison of the results obtained under standard conditions, i.e. an agitation speed of 7500 rpm and a temperature of 30 °C, and that obtained when the agitation speed was decreased. It should be noted that the only difference between these two types of experiments is a decrease in impeller speed after 20 minutes of agitation. Each line on the graph is an average of 20 tests.

From Figure 4.13 it can be seen that there was a decrease in the amount of undersize capsules produced when the impeller speed was reduced. The proportion of capsules below 2 microns was reduced to 19.71%, from 24.20% produced at standard conditions. Figure 4.12 shows that there was an increase in the average capsule diameter, from 5.12 to 5.89 microns, and the oversize capsules increased from 1.63 to 1.89%, as shown in Figure 4.14. There was concern as to whether these increases would be significant during the microcapsule coating process. To test the results obtained in the laboratory, a trial run was conducted at the chemical plant in Mondi. In order for the trial to be successful, the laboratory impeller speeds of 7500 and 7200 rpm had to be converted to suite the plant impeller. The plant impeller speed was expressed as a percentage of the maximum speed and hence it was reduced by the same ratio. This corresponds to a proportional drop in impeller tip speed. Appendix B illustrates this further.

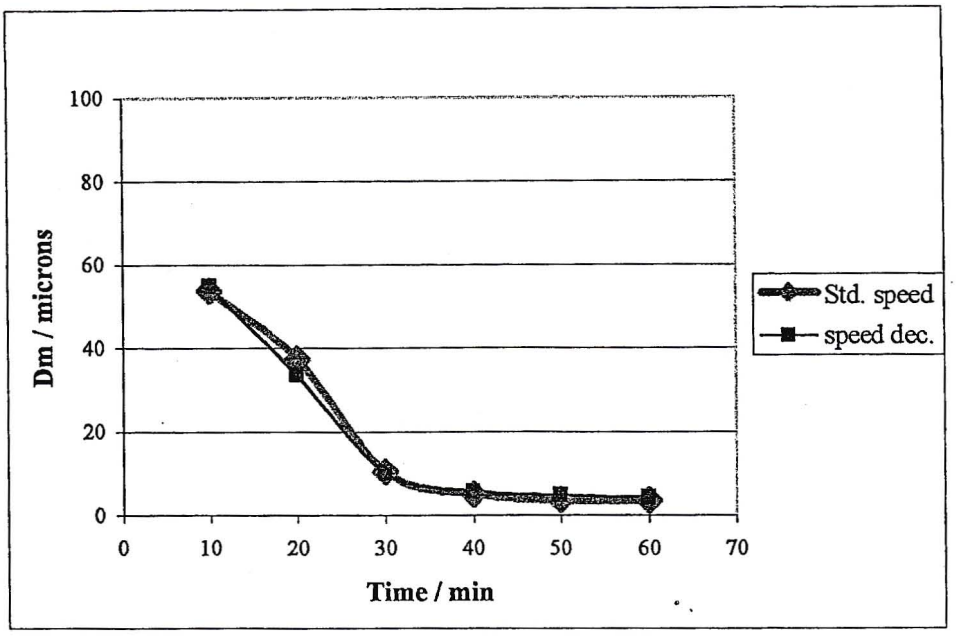


Figure 4.12: Effect of reduction in agitation speed showing the mean capsule diameter

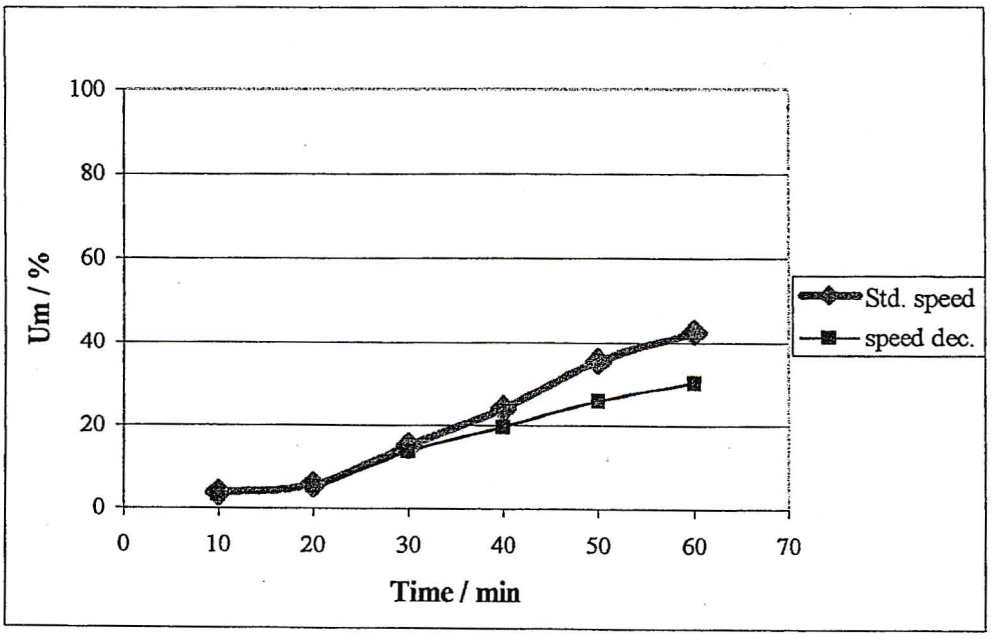


Figure 4.13: Effect of reduction in agitation speed showing the mean undersize

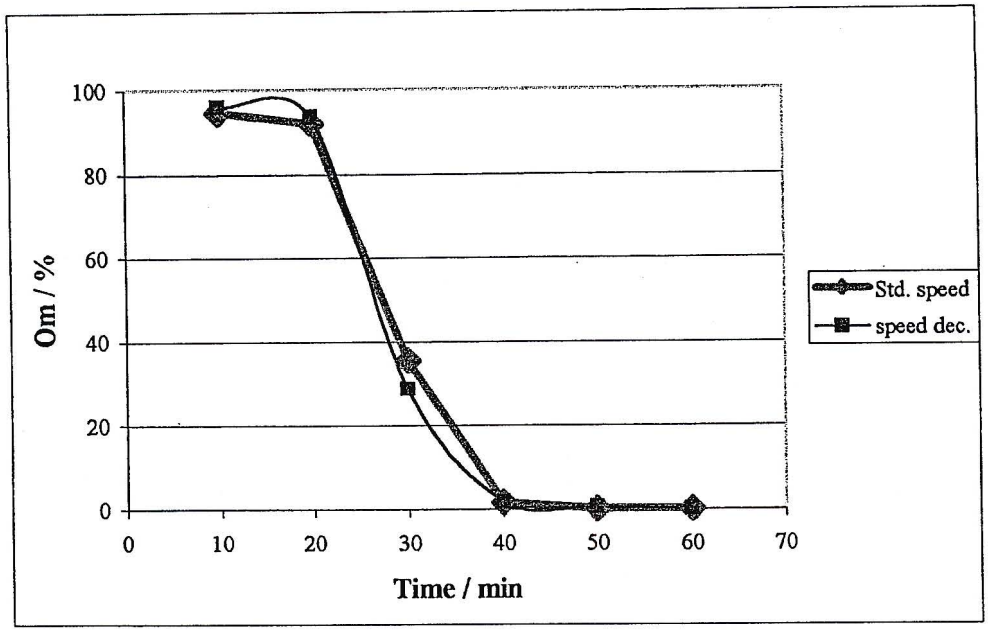


Figure 4.14: Effect of reduction in agitation speed showing the mean oversize

The agitator speeds are summarised below.

Table 4.3: Laboratory and plant impeller speeds

Lab impeller - 0.045 m	Plant impeller - 0.540 m
7500 rpm ~ 18 m/s	75% ~ 775 rpm ~ 22 m/s
7200 rpm ~ 17 m/s	70% ~ 735 rpm ~ 21 m/s

The agitation speeds were determined empirically in the above manner since the plant and laboratory emulsifying tanks were not geometrically similar (i.e. Equation 2.1 in Chapter 2 was not used).

Having found operating speeds, which brought about a decrease in the undersize capsules, the trial run was conducted at the Mondi plant. A summary of the results obtained is shown in Tables 4.4 and 4.5.

Table 4.4: Trial run results at the Mondi plant

	< 2 micron capsules (%)	> 10 micron capsules (%)	Average size (D)
75% for 20 min.	6.16	93.84	31.85
70% for 20 min.	18.39	13.45	7.09
70% for a further 15 min.	23.83	1.59	4.79

Table 4.5: Comparison to current production

	Average size (%)	< 2 microns (%)	> 10 microns (D)
Current production	4.40	25.70	0.73
Trial	4.79	23.83	1.59

For the trial run, the increase in the percentage of capsules less than 2 microns after capsule formation, appears to result from breakage of capsules by the impeller into smaller particles. The use of a lower impeller speed for this phase did result in a small reduction in the proportion of undersize, but an increase in the capsule diameter. However the percentage of capsules larger than 10 microns increased slightly from 0.73 to 1.59%. This increase was not considered to be a problem since the reels of paper coated with the microcapsules were within specification. It was still, however, not significant enough to lead to monetary savings. The use of impeller speeds below 70% was not considered, as previous experience had shown that the emulsion separated into clusters. This phenomenon attributed to a lack of sufficient emulsion viscosity.

4.3.5 Effect of emulsification time

According to Sanchez et al. [1998], who prepared emulsions using a 75-wt % sunflower oil, the evolution of the DSD curves with emulsification time were different at different intervals. The curves were unimodal at intermediate times but became bimodal after a while (after the

emulsification period). This trend was observed in this project when samples were taken at regular time intervals, during emulsification, to determine the particle sizes. See Appendix A, Figures A1 to A6. Barnes [1994] also observed a similar trend. This lead to the concept of reducing the production of fine droplets, by reducing the impeller speed after the initial emulsification.

4.3.6 Effect of the baffle width

Baffles are needed when mixing liquids of low viscosity to prevent vortex formation and the inclusion of air. They provide barriers to the liquid motion, which destroy the vortex, and produce a flow pattern conductive to good mixing (Nagata [1975], Stephens & Goodes [1982], Uhl & Gray [1966] and Ulbrecht & Patterson [1985]. This was observed during experimentation where the size of the baffles was increased. Although the baffles ensure homogeneity of the emulsion, by providing a flow pattern that carries throughout the entire batch, excessive baffling is possible. This is termed "overbaffling", which may result in a poor system performance by localising the mixing (Oldshue [1983], Holland & Chapman [1997] and Ram et al. [2000]). This was also observed during experimentation.

In order to conduct the experiments a new laboratory tank was made. It was constructed of perspex, in order to view the mixing effect at different speeds. It was also was much larger than the previous tank, so that the baffle size could be increased. Figure 3.5, Chapter 3, shows a picture of the tank. Three baffles were used since the plant emulsifier tank and the previous laboratory tank had three. The tank was much lighter than the original steel tank used previously, because of the low density of perspex. At higher impeller speeds the tank vibrated. Also, during the experiments the large vortex formed at the high agitation speeds, when no baffles were used, caused the emulsion to overflow. A suitable impeller speed of 5540 rpm was then chosen, which was the highest speed obtainable, before vibrations occurred. Since this speed was lower than the standard speed used for previous experiments, the desired results were not obtained after 40 minutes. Better results were obtained after 60 minutes. This was not a problem since during production at the plant; the capsules are emulsified for 60 minutes, if the desired results are not obtained within 40 minutes. Initially the emulsion was produced with no baffles in the tank. This was done to observe the vortex formation and compare the results obtained when the baffles were added. The baffle sizes included 5, 10 and

15 mm. There were no variations to the standard operating procedure used for these experiments. Each experiment was repeated 10 times and the data was averaged.

Figure 4.16 shows a decrease in the amount of capsules produced below 2 microns in diameter, as the size of the baffles increased. This meant that there was not enough shear supplied to the emulsion or that coalescence was occurring in the stagnant zones. Figure 4.15 shows an increase in the capsule diameter, as the baffle size increased, and Figure 4.17 shows an increase in the amount of oversize capsules produced. These results are consistent with "overbaffling", which is explained with the aid of the Figure 4.18. Experimentation with the 5 mm baffles gave undesirable results with an average capsule diameter of 5.92 microns, a percentage undersize of 25.68% and a percentage oversize of 4.74%. The capsule diameter and the oversize did not fall within the specified range, even when no baffles were used. This implies that the design of the larger vessel was not appropriate for the impeller size and speed and that, for example, a higher impeller speed may be required for the larger vessel.

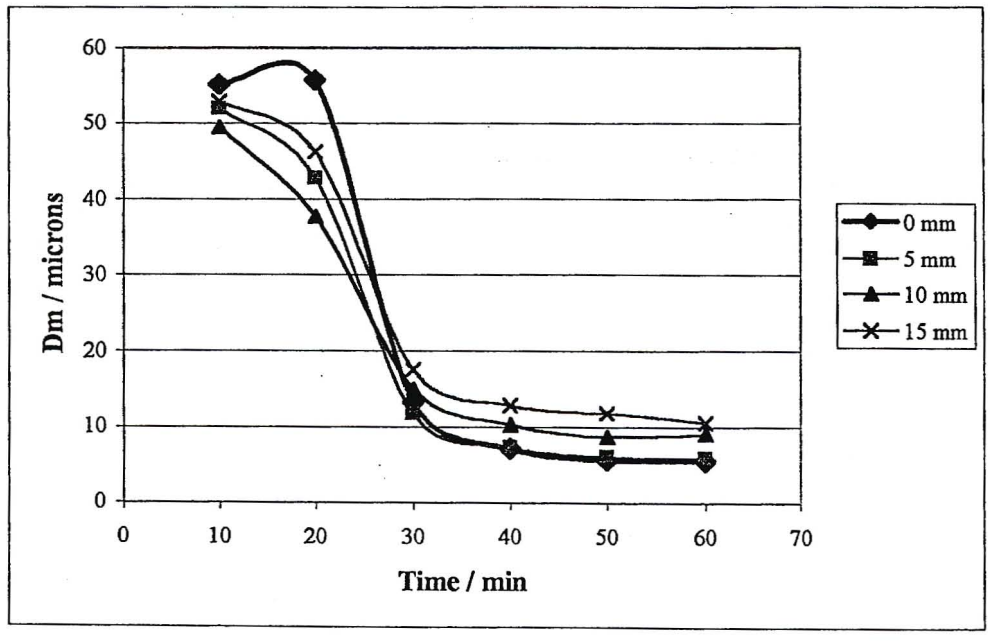


Figure 4.15: Baffle width variation showing the mean capsule diameter

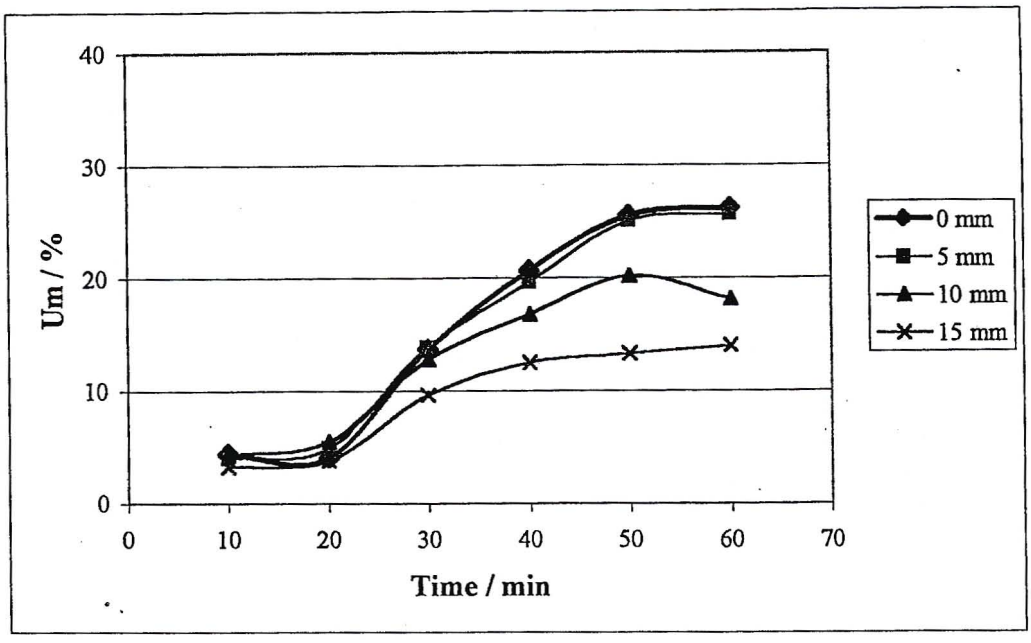


Figure 4.16: Baffle width variation showing the mean undersize capsules

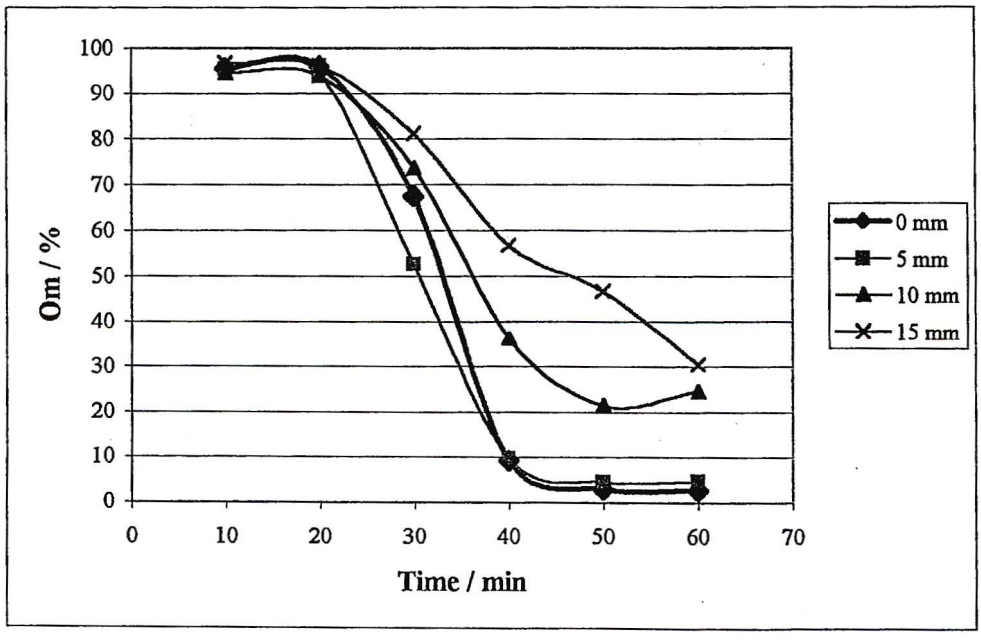


Figure 4.17: Baffle width variation showing the mean oversize capsules

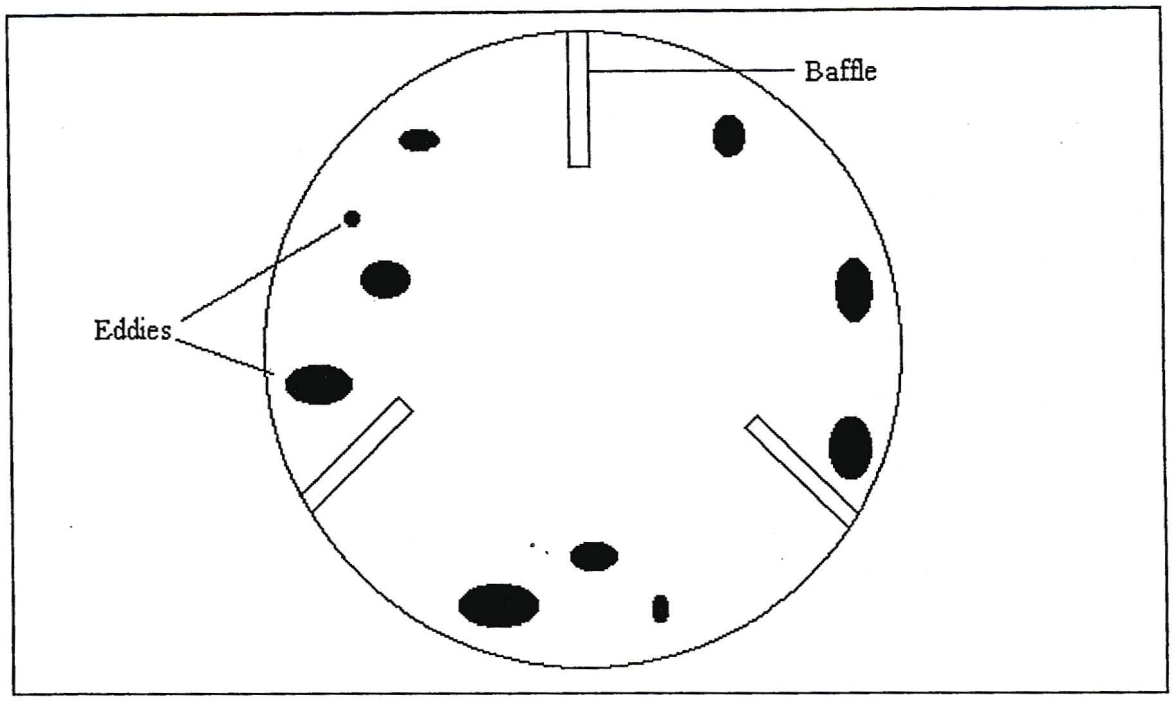


Figure 4.18: Top view of the laboratory emulsifier tank

With very large baffle widths, a relatively stagnant zone between the baffles is produced, compared to the zone near the center of the tank, where the impeller is situated. Eddies, which are large lumps of the emulsion, are formed in the stagnant zone, since the circulation of the liquid is low. This contributes to the large capsule sizes and the small amount of undersize capsules produced.

4.3.7 Reproducibility of results

The experiments done thus far were all repeated a number of times and the averages of the results were discussed. A statistical meaning, (Brooks & Dick [1951] and Skoog et al. [1996]), was given to the experiments that showed the most promising results.

4.3.7.1 The "standard" experiment

The standard experiment, i.e. the experiment with conditions of 7500 rpm agitation speed and an emulsification temperature of 30 °C (in the metal vessel), was done several times in order to be certain that the results were reproducible. The upper and lower limits of the first standard deviation, +S1 and –S1 were calculated.

Figures 4.19, 4.20 and 4.21 shows the range over which the average capsule diameter, percentage of undersize and the percentage of oversize capsules respectively. The +S1 and –S1 bracket represents 68.3% certainty that the results of further experiments will lie in this range. From Figure 4.19 one can see that the results for the average capsule diameter were very reproducible at 40 minutes. As discussed earlier, the results only became significant after about 40 minutes. The undersize graph, Figure 4.20, also shows reproducible results at 40 minutes. The wide distribution of data after 40 minutes suggests that the results were not reproducible. Explanations of the possible reasons for the spread of the data are given in this Section. Figure 4.21 also shows very reproducible data after 40 minutes.

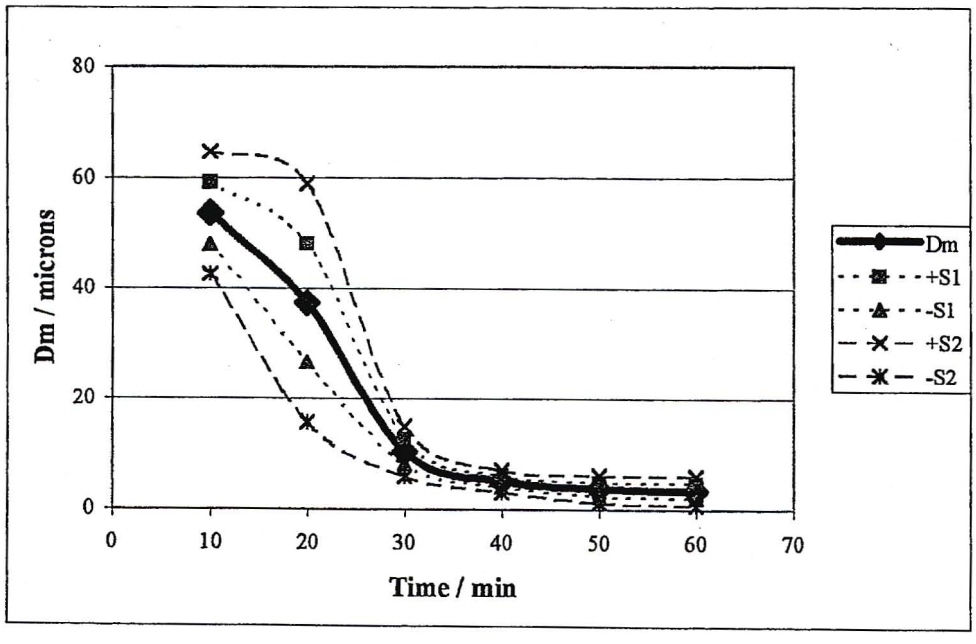


Figure 4.19: Reproducibility of results at 30 °C showing the mean capsule diameter

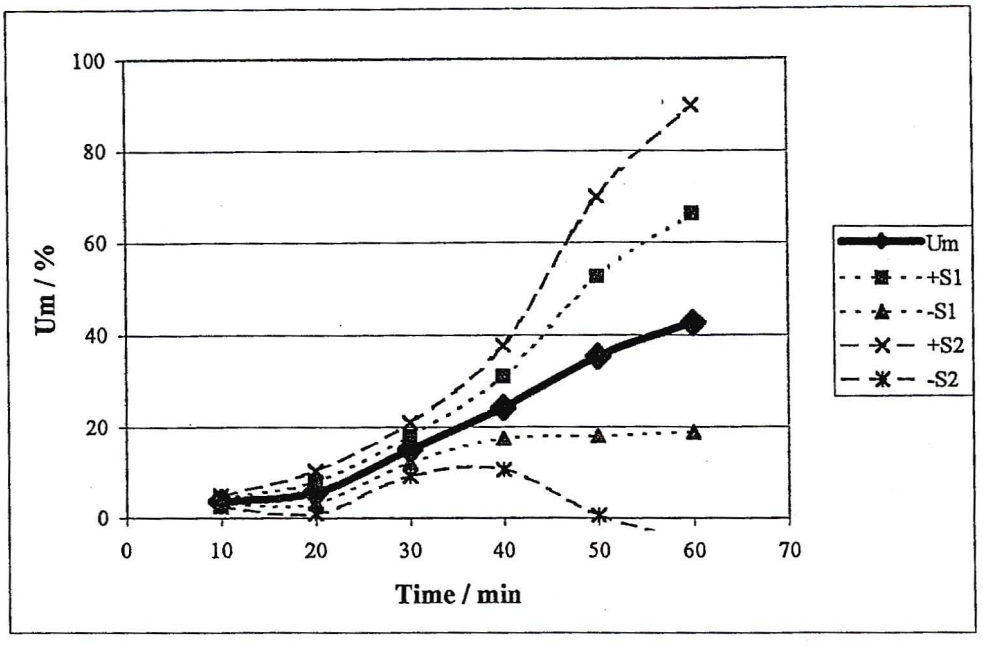


Figure 4.20: Reproducibility of results at 30 °C showing the mean undersize capsules

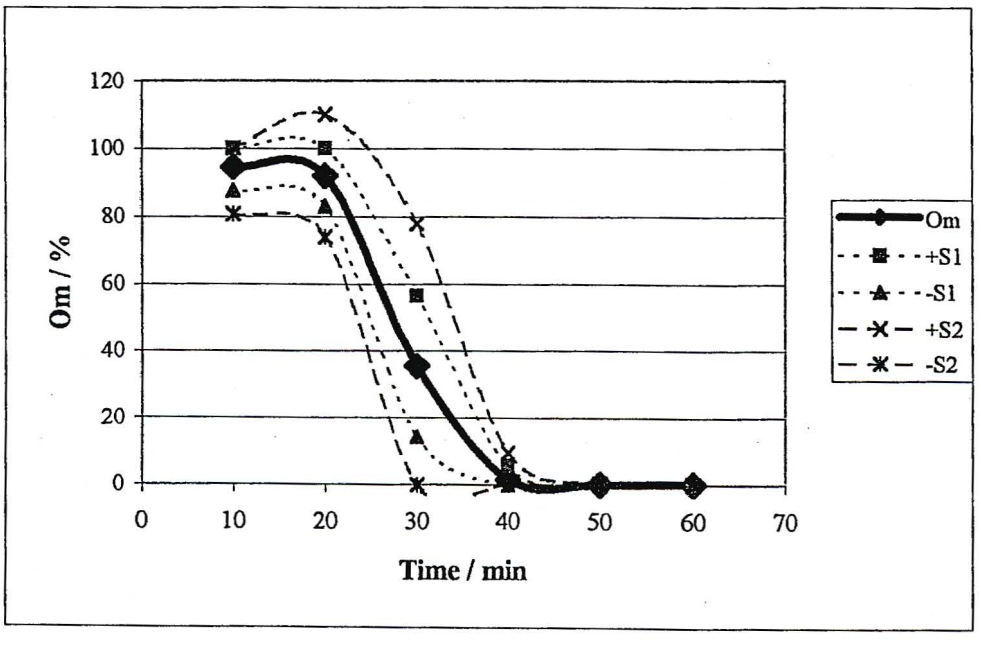


Figure 4.21: Reproducibility of results at 30 °C showing the mean oversize capsules

4.3.7.2 The effect of temperature

Experiments at temperatures ranging from 22 to 40 °C were each done 20 times. Figure 4.22 show that the results for the capsule diameter were reasonably reproducible. The reproducibility decreased at temperatures below 25 °C. As discussed earlier, the emulsion was very unstable at the lower temperatures and this could have caused the wider spread of data. Figures 4.23 and 4.24 also show a fair distribution of data within the 68.3% certainty bracket.

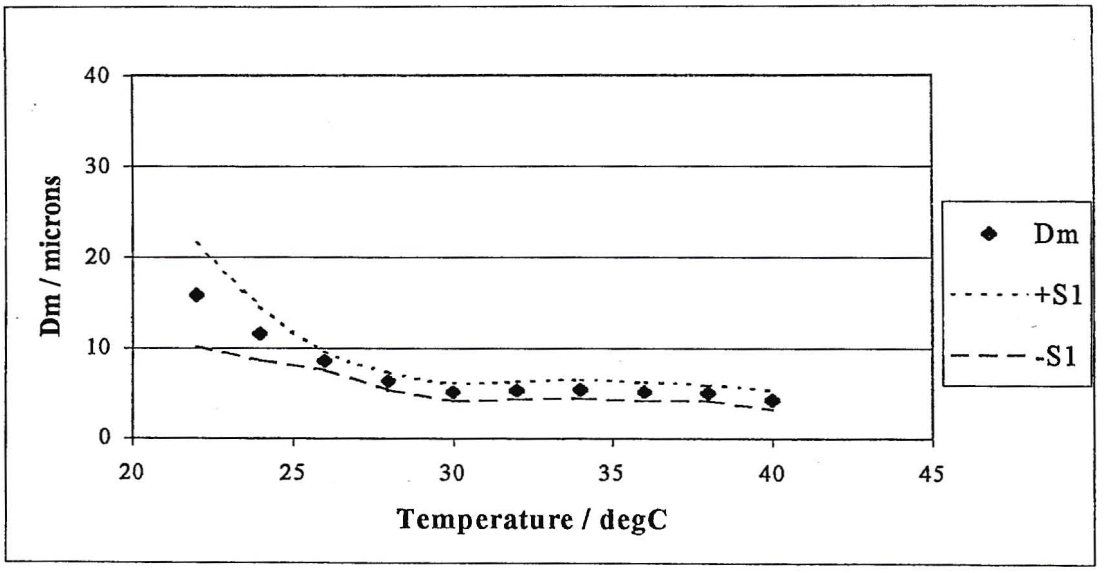


Figure 4.22: Effect of temperature on the spread of data for mean capsule size after 40 minutes of agitation

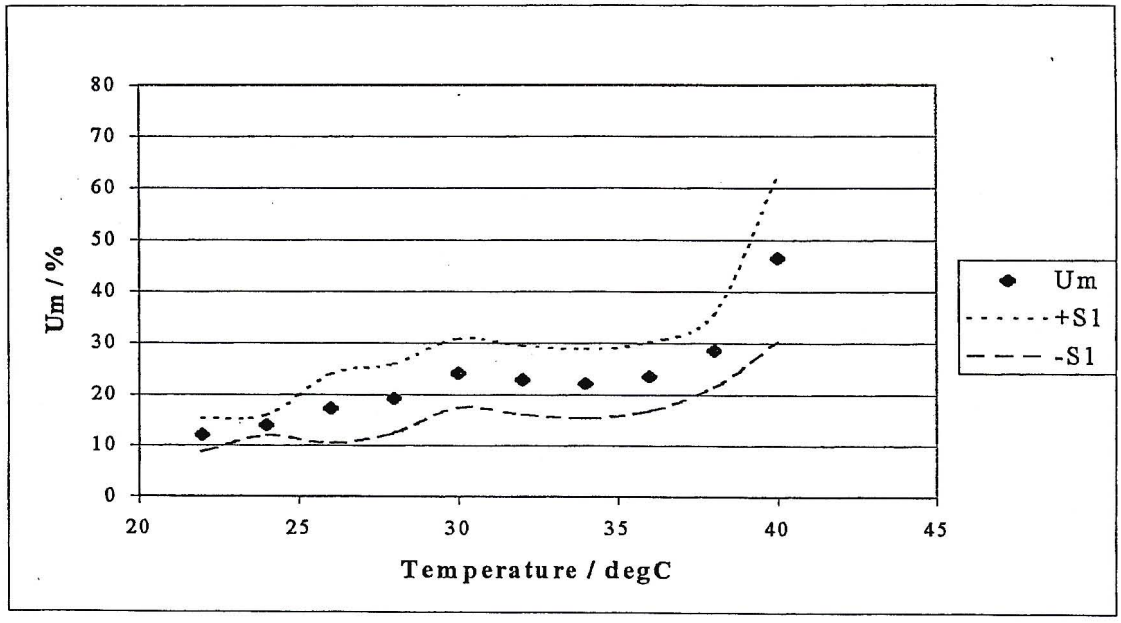


Figure 4.23: Effect of temperature on the spread of data for undersize determined after 40 minutes of agitation

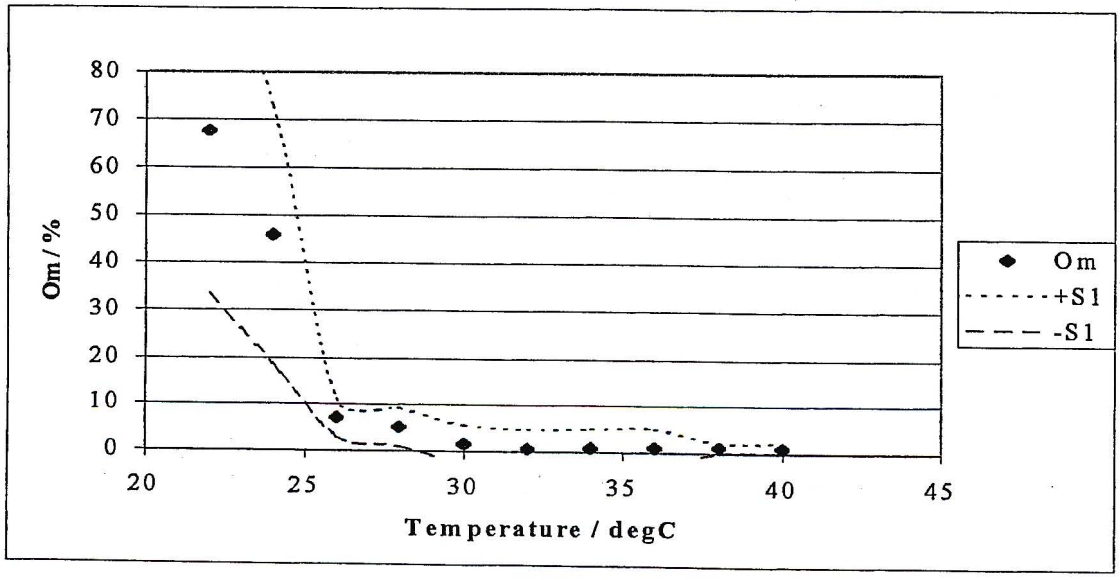


Figure 4.24: Effect of temperature on the spread of data for determination of percent oversize after 40 minutes of agitation

4.3.7.3 Reduction in agitation speed

Since the experiments with a reduction in agitation speed were the most successful experiments, the data obtained from them will be discussed in more detail.

The variation of the results during the first 30 minutes of emulsification, in Figure 4.25, could be caused by many factors. The impeller speed could be one of the factors since the Silverson mixer is a very old model and fluctuations in speed are normally experienced. As the polymerisation reaction proceeds the emulsion becomes more viscous. The impeller speed slowly decreases with the increase in viscosity, when it ought to remain constant. The chemicals used to produce the capsules in the laboratory were sometimes fresh chemicals just recently supplied to Mondi, or sometimes they were stored for some time in the cupboard, before use. This could be one of the factors influencing the initial variation in results. After about 30 minutes, the emulsion became much more viscous and insensitive to temperature changes and small differences in the impeller speed. However, when the variation is expressed as a fraction of the value, it remains relatively constant. This allows the emulsion to be more stable, hence the reproducibility of the results is high in this region. Figure 4.26 shows that the percentage undersize is initially small, but that after 40 minutes the data became progressively more scattered.

Figure 4.27 shows that the reaction is complete after 40 minutes and time have little effect on the emulsion thereafter. Between 10 and 40 minutes there is a larger deviation of the results from the mean. This is probably due to the fluctuation in temperature whilst the reaction is occurring. Heat is added to the emulsion during agitation and this increases the temperature. Cold water is constantly added in the outer jacket of the vessel to maintain the temperature at 30 °C. Sometimes the temperature may drop below 30 °C when the cold water is added. Since the system is very sensitive to temperature, these small fluctuations could vary the results. As explained earlier, after 40 minutes the emulsion is viscous and more resistant to temperature changes.

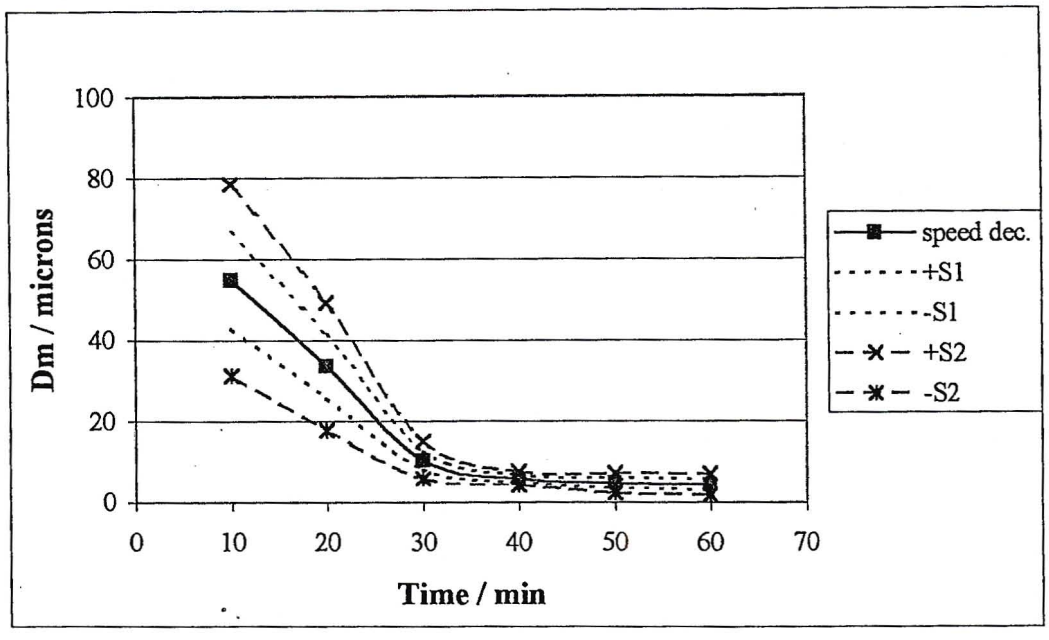


Figure 4.25: Reduction in agitation speed showing the reproducibility of results for the mean capsule diameter

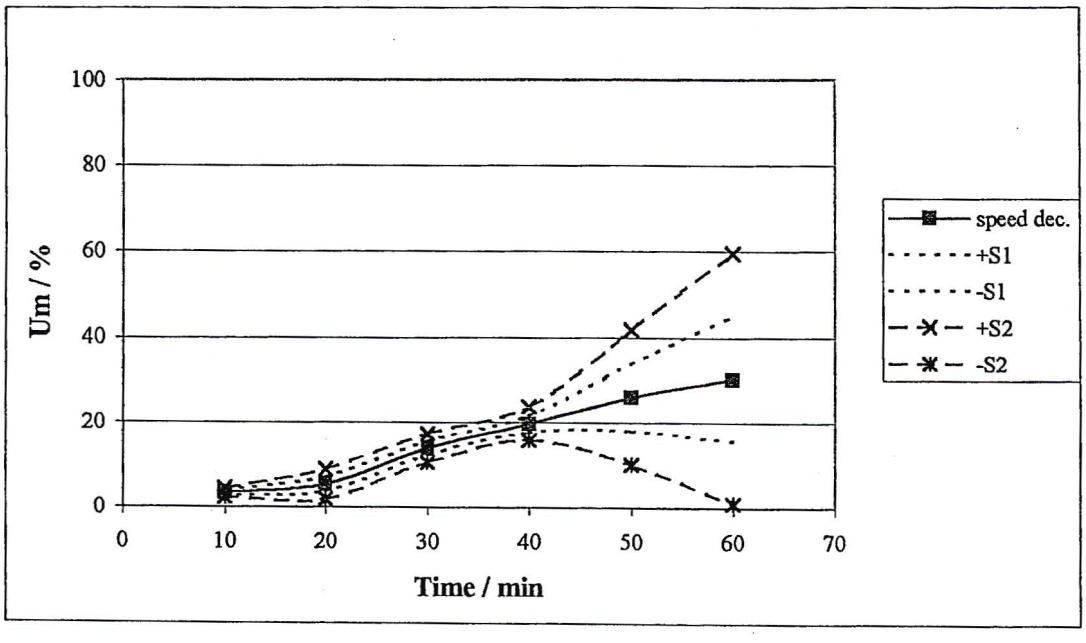


Figure 4.26: Reduction in agitation speed showing the reproducibility of results for the mean undersize capsules

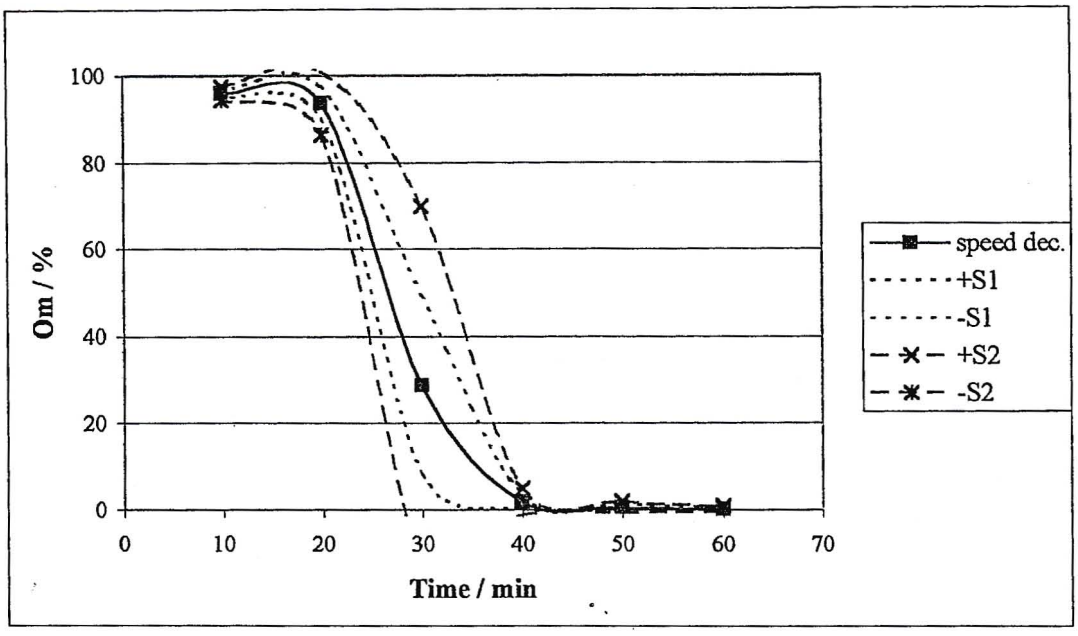


Figure 4.27: Reduction in agitation speed showing the reproducibility of results for the mean oversize capsules

4.3.8 The scaled-down laboratory tank

The new steel tank, which had dimensions exactly one-tenth to that of the plant tank (including baffles), worked well in producing the microcapsule emulsion. The only change to the standard operating procedure that was made when using this tank was the agitation speed. Instead of 7200 rpm, which was previously adopted as a standard speed, the scale-up rule of Equation 2.1, Chapter 2, was used. The new standard agitation speed was now 7750 rpm. This speed provided the best match in terms of average diameter and size distribution to the plant capsules.

The results of the initial trial runs done in this tank can be seen in Figures 4.28 to 4.30

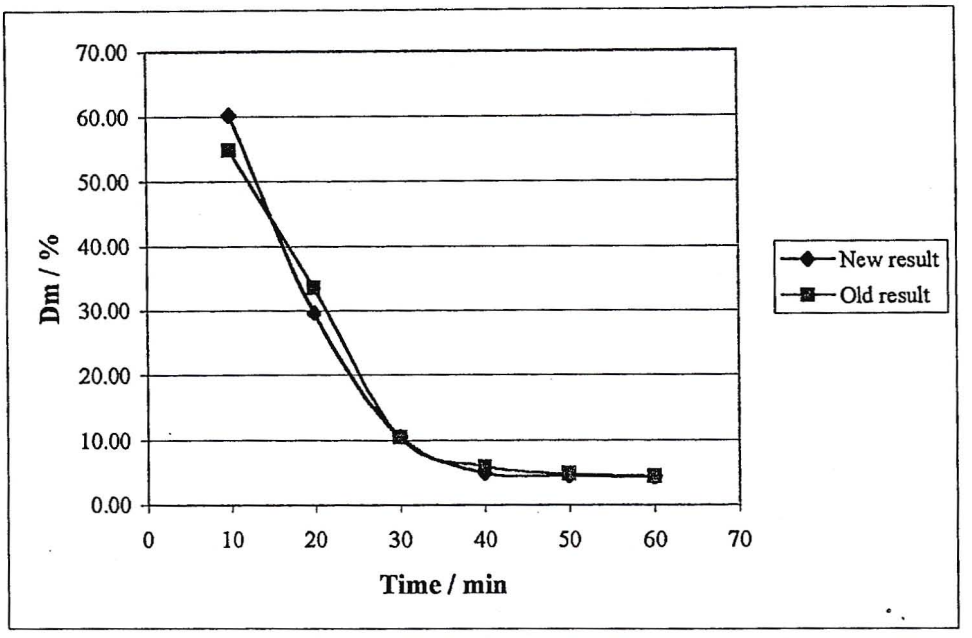


Figure 4.28: Comparison of new and old laboratory tank – mean capsule diameter

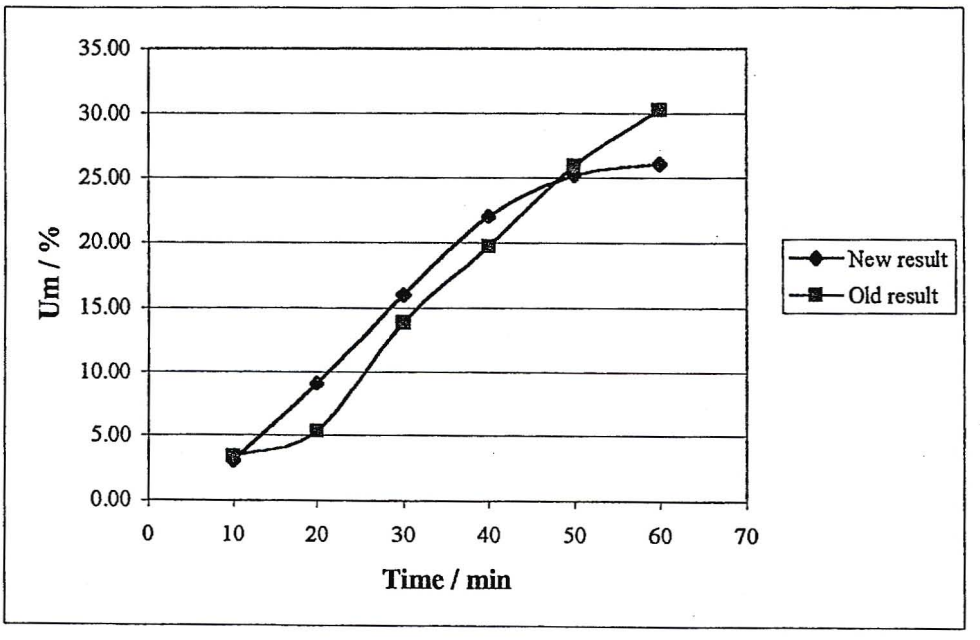


Figure 4.29: Comparison of new and old laboratory tank – mean undersize

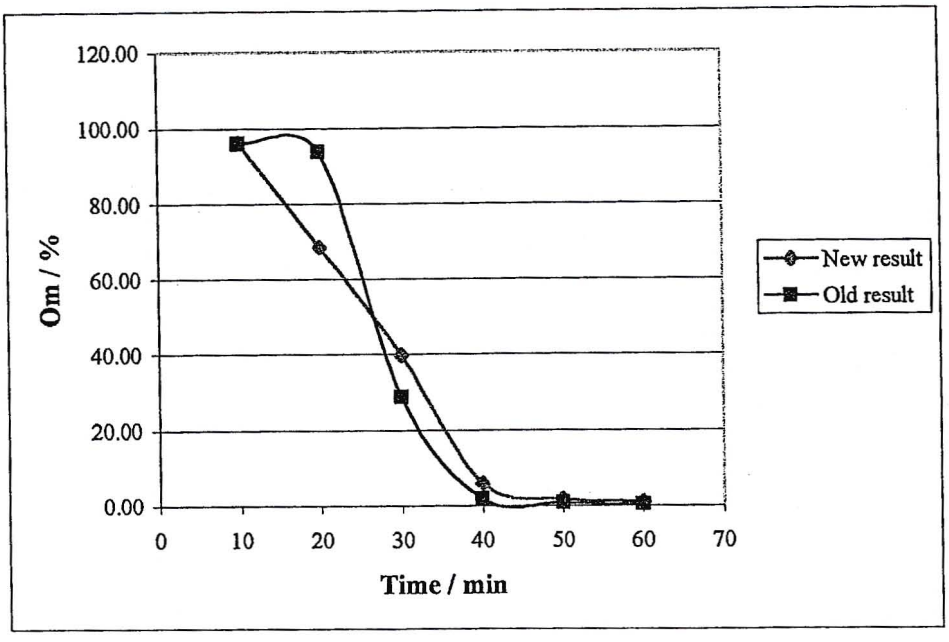


Figure 4.30: Comparison of new and old laboratory tank – mean oversize

4.3.9 The Emulsion Inversion Point (EIP) method

The Emulsion Inversion Point (EIP) method, as discussed in Chapter 2, proved unsuccessful when used to produce the microcapsules, although Uniqema, using different reactants, has already proved its success. This is probably because the capsule walls have been developed, and tend to grow in clusters, rather than being broken down. Therefore a higher shear is required to break the emulsion down further.

The following observations were recorded which made the process unsuitable:

- Instead of a colourless emulsion being produced, a light purple colour was noticed.
- After the emulsification process, the oil was seen to coalesce into a separate layer, showing that the emulsion did not mix well.
- The capsule size after emulsification was too big, greater than 100 microns.

Figures 4.31 to 4.33 shows the results obtained during the EIP method, as compared to the normal method used at Mondi.

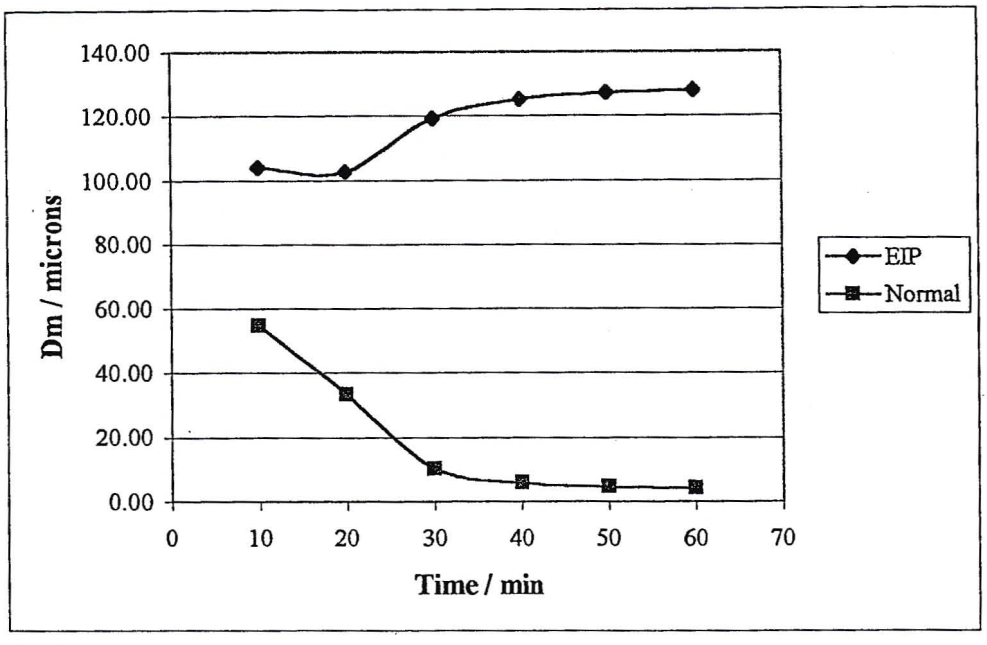


Figure 4.31: Comparison of the EIP method to the normal method – mean capsule diameter

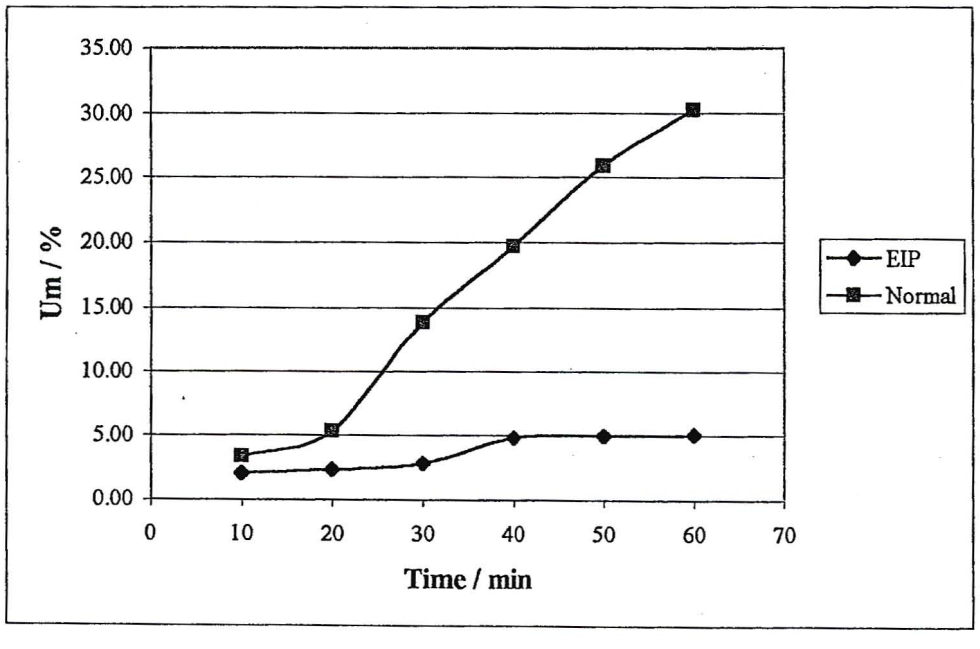


Figure 4.32: Comparison of the EIP method to the normal method – mean undersize

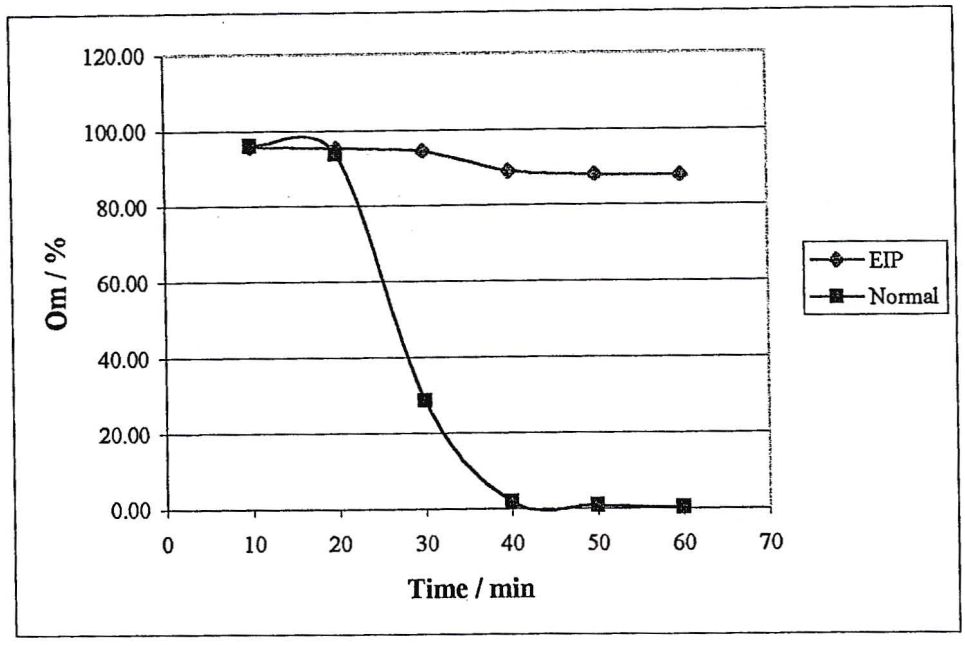


Figure 4.33: Comparison of the EIP method to the normal method – mean oversize

4.3.10 Viability of a different surfactant

Since the trade information related to Lupasol is very limited, it was difficult to obtain a suitable alternative of a similar chemical nature. Table 4.6 shows the chemical companies that were approached, and which were unable to match the properties of Lupasol. Laboratory tests on Lupasol, conducted at the University of Natal, measured an HLB of Lupasol of approximately 15. Based on this HLB number, and the limited available information on Lupasol, only one surfactant, of similar HLB, Atpol E1231, was obtained from ICI Surfactants and tested at Mondi. Normal operating procedures and conditions were used with the exception of Lupasol, which was replaced by the alternative being tested.

Atpol E1231

The test was futile since Atpol E1231 exhibited poor characteristics towards the microcapsule emulsion. The following was observed during experimentation:

Table 4.6 Companies approached for surfactants

Company	Location
Labco. Supplies	Durban
Lab. Consumables	Durban
Labsol Consultants	Durban
Uniqema	Johannesburg
Chemical & Industrial Marketing	Johannesburg
Chemimpo	Durban
Chemnet	Durban
Chemserve Tech. Products	Durban

- The emulsion turned into a light green colour, instead of the colourless solution normally produced.
- Too much of foam was generated.
- The emulsion became too viscous.

For this reason, the testing of the particle size was not done. It proved to be difficult to find surfactants with similar properties to that of Lupasol. The only available information is that Lupasol is a polyacrylic sulphonic acid derivative, according to Tessmer, [1999], and that its HLB value lies in the range of 14-15, which was determined in the laboratory. Chemical companies required more information in order to provide samples of alternative surfactants.

4.3.11 Power measurement

4.3.11.1 Impeller power

A basic turntable, attached to a load cell and a digital display, was constructed. The digital display gave a reading of the force produced, by the rotational motion of the tank, when it was placed on top of the turntable. This allowed for the calculation of the torque produced, by the following equation:

$$\text{Torque } (\tau) = F \times r \qquad (4.2)$$

Where F is the force in Newtons, and r is the radius of the turntable in meters, 0.21 m. Hence the power given off by the impeller in the tank was found by:

$$\text{Power } (P) = [(2 \pi N)/60] \times \tau \qquad (4.3)$$

Where N is the rotational speed of the impeller (rps). Initial tests were done with water only as the mixing medium, in order to test the load cell, before applying it to the emulsion. Table 4.7 shows the results obtained.

Table 4.7: Power calculated with water as the medium

Speed (rpm)	Load cell (kg)	Force (N)	Torque (N.m)	Power (W)
3270	0.00	0.00	0.00	0.00
5000	0.00	0.00	0.00	0.00
5540	0.00	0.00	0.00	0.00
6100	0.02	0.20	0.02	13.15
6600	0.03	0.29	0.03	21.34
7200	0.05	0.49	0.05	38.79
7500	0.07	0.69	0.07	56.57
7750	0.09	0.88	0.09	75.16

An increase in power can be clearly seen as the agitation speed increased. Thereafter tests were done using the microcapsule emulsion as the mixing medium. Initially a constant agitation speed was used, and Tables 4.8 and 4.9 shows the results obtained. Figure 4.34 shows how the power increases, as the speed remains constant. During the emulsification process the viscosity of the emulsion increases with time. Figure 4.34 therefore shows how the power increases with increasing viscosity.

Table 4.8 Power calculated with the emulsion as the medium – constant agitation speed

Time (min)	Speed (rpm)	Load cell (kg)	Force (N)	Torque (N.m)	Power (W)
0	7750	0.11	1.08	0.11	91.86
5	7750	0.11	1.08	0.11	91.86
10	7750	0.12	1.18	0.12	100.21
15	7750	0.14	1.37	0.14	116.92
20	7750	0.15	1.47	0.15	125.27
25	7750	0.15	1.47	0.15	125.27
30	7750	0.15	1.47	0.15	125.27
35	7750	0.16	1.57	0.16	133.62
40	7750	0.16	1.57	0.16	133.62
45	7750	0.16	1.57	0.16	133.62
50	7750	0.16	1.57	0.16	133.62
55	7750	0.17	1.67	0.17	141.97
60	7750	0.17	1.67	0.17	141.97

Table 4.9: Power calculated with the emulsion as the medium – varying agitation speed

Speed (rpm)	Load cell (kg)	Force (N)	Torque (N.m)	Power (W)
3270	0.00	0.00	0.00	0.00
5000	0.00	0.00	0.00	0.00
5540	0.01	0.10	0.01	5.97
6100	0.05	0.49	0.05	32.87
6600	0.09	0.88	0.09	64.01
7200	0.13	1.27	0.13	100.86
7500	0.16	1.57	0.16	129.31
7750	0.17	1.67	0.17	141.97

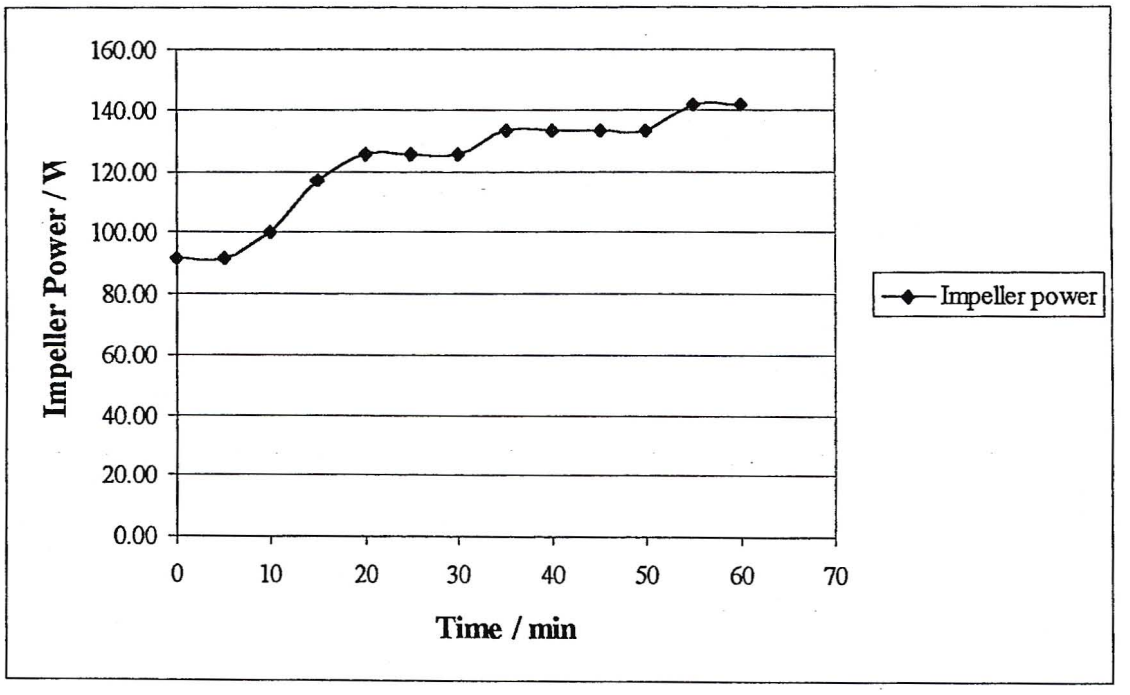


Figure 4.34: Graph of impeller power versus time for power measurement

From the above graph it can be clearly seen that the power in the system tends to stabilise as time increases. This result was not expected as size distribution data showed an ongoing production of undersize particles. The encapsulation of the oil droplets after a certain period probably limits the production of ultra-fine particles, which would cause changes in viscosity.

4.3.11.2 Power number

Using the results obtained in Table 4.8, it was decided to calculate the dimensionless power number, Np, for the laboratory impeller. Since the emulsion is stable after about 60 minutes of emulsifying, the power calculated after this time was used, i.e. 141.97 W. The power number is defined by the following equation:

$$Np = P / \rho N^3 Di^5 \qquad (4.4)$$

Where ρ is the density of the emulsion (kg/m^3), N is the rotational speed of the impeller (rps) and Di is the impeller diameter (m). The value of the density, according to the plant personnel, is approximately 1000 kg/m^3. Np was found to be 0.357 for the laboratory impeller. It should be noted that the laboratory impeller was not geometrically similar to the plant impeller and hence the normal laws of scale-up do not apply. For example, the angled blades were not similar in size to the blades on the plant impeller. In view of the fact that similar emulsions were produced at equivalent tip velocities, it may be concluded that the turbulence was similar. One interpretation of this phenomenon is to assume that the power number was the same. Therefore using Np = 0.357, and equation 3, the calculated power for the plant impeller was found to be 35 kW. This appears to be a reasonable approximation as the plant variable speed motor as a rating of 45 kW and the speed was 75% of the maximum speed. Unfortunately it was not possible to measure the power drawn by the plant impeller during normal operation. Just as a comparison, the power per unit volume of the two systems were calculated as follows:

$$(P / V)_{plant} = 11{,}78 \text{ kW/m}^3$$

$$(P / V)_{lab} = 47{,}00 \text{ kW/m}^3$$

This was expected since laboratory impellers tend to use a higher power per unit volume. The above calculation of the power of the plant impeller was done assuming Rule 1 of Chapter 2 and clearly Rule 2 does not apply because of the lack of geometric similarity.

4.3.11.3 Causes of error in power measurements

There are many potential sources of errors in power measurements. The two most relevant ones to this study are discussed below, with reference to Nagata [1975]. It is important to acknowledge these errors when considering the results.

Errors caused by friction

Power losses may be obtained when there is mechanical contact of the impeller shaft with any fixed part, typically bearings and gearboxes. The latter was not applicable with a DC variable speed motor.

Errors caused by static friction

Static friction is caused by the moving part contained in the torque measuring system like the bearing of the turntable in Figures 3.8a and b, Chapter3.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Many methods exist to produce micro-emulsions of uniform particle size and good stability, but they have certain limitations. The methods discussed are common in industry and they produce capsules, which are within the existing specifications, but not as sensitive as the process for carbonless paper.

5.1 The micro-encapsulation processes

As discussed in Chapter 2, some of the more popular methods for microcapsule production are not suitable for carbonless copy paper production. The methods researched were solvent evaporation, coacervation, nozzle type processes and stirred tank processes. Solvent evaporation produces ill-defined microspheres and is therefore not suitable for carbonless paper. The Wurster process, described in Figure 2.2, shows a common industrial process used to encapsulate individual particles. This is a very efficient process for producing capsules in the range of 4-6 microns, but a very small nozzle diameter of about 2 to 6 microns is required. This is uncommon in industry since blockages of the nozzle can easily occur.

The rotational suspension separation method, illustrated in Figure 2.2, is another encapsulation process that gives a narrow distribution of particle sizes. However, this process is used in a suspension of water. The colourformer oil has a lower density than water and will rise to the surface. Therefore there would be difficulties experienced during the encapsulation process.

The process of coacervation is also a widely practiced method, used mainly for microcapsule production for perfumes, flavour in foodstuff and agrochemicals. Coacervation has also proved to be successful for carbonless paper production but requires the use of very different raw materials and equipment. This could prove to be costly and Mondi would prefer to continue with the existing process and modify it where possible.

After reviewing all the literature it was concluded that the most efficient method to produce microcapsules for carbonless paper is the stirred tank emulsification process, which is the current process at Mondi.

5.2 Raw materials

The solvent used in the present process, di-isopropylnaphthalene has become well accepted in the market for carbonless paper. It combines all the required chemical and physical properties, with very low toxicity and environmental compatibility (Stadelhofer & Zellerhoff [1989]). It is recommended that the use of this solvent be continued.

There are many alternatives to formic acid, the polymerisation initiator, but it does not affect the final product specifications, and testing the alternatives would be futile. Formic acid was also shown to be one of the better polymerisation initiators for the microcapsule process.

5.3 Optimisation of process variables

5.3.1 Influence of the agitation speed during the emulsification phase

The following conclusions were drawn during experimentation with the agitation speed:

- An increase in the speed of the agitator will lead to a smaller average capsule diameter. This will also increase the amount of smaller capsules produced, resulting in a wider size distribution.
- A decrease in agitator speed, for the entire duration of emulsification, will produce a larger average capsule diameter. Although a smaller amount of undersize particles will be produced, the size distribution will not fall in the desired range, with an unacceptable proportion of particles larger than 10 microns.
- A decrease in the agitator speed half way through the emulsification phase will produce desirable capsule sizes, as well as a narrower size distribution. It is recommended that the emulsion should be produce at normal operating speed, for the first 20 minutes, and thereafter the speed should be reduced by 5%, for the rest of the emulsification period.

5.3.2 Influence of the emulsification temperature

The standard operating temperature at the chemical plant at Mondi is 30 °C. Temperatures above and below this temperature were investigated and the following conclusions were drawn:

- Undesirable capsules will be produced at temperatures below 30 °C. The desired capsule size will not be reached after 40 minutes, which is the standard operating time. Although the percentage of undersize capsules will be low, the emulsion will not be viscous enough to be coated on paper and un-encapsulated oil will be seen in the final emulsion. The proportion of oversize capsules will also be too high.
- Producing capsules at temperatures above 30 °C will not result in many changes in the undersize and oversize capsules. The average capsule diameter will increase by a small amount and this may have a negative effect on the smudging of the paper.
- Temperatures higher than 38 °C are not desirable since the reaction rate becomes too high. The emulsion will be too viscous to be coated on paper. 30 °C proved to be the most suitable temperature to produce the emulsion.

5.3.3 Influence of the emulsification time

According to Sanchez, the evolution of the droplet size distribution curves with emulsification time was different. The curves were unimodal at intermediate times but bimodal at longer times, for a single run. This trend was observed in this project (see Appendix A). The process of emulsification of oil for microcapsules used in carbonless copy paper requires approximately 40 to 60 minutes, in order to form a stable emulsion. During this time a bimodal distribution was always observed. The following conclusions were made about the effect of the emulsification time on the microcapsules:

- An unstable emulsion will be produced for an emulsification time less than 40 minutes. The capsule diameter will be too large, there will be too much oversize capsules and the size distribution will be too wide. The polymerisation reaction will also not be complete and the emulsion will not be suitable for coating on paper.
- The polymerisation reaction is sufficiently complete, after 40 minutes of emulsification, for the emulsion to be coated on paper. The specifications of the capsules lie within the preferred range.
- An emulsion with a very high viscosity is produced if it is emulsified for more than an hour. Agglomeration of the particles also occurs if the agitation speed remains unchanged.

The polymerisation agent (formic acid) should only be added to the emulsion once the initial reagents are thoroughly mixed. Judging from the colour and viscosity of the emulsion, as mentioned in Tessmer [1999], the emulsion does look well mixed when the current Mondi procedure is used. Therefore the moment at which the formic acid is added, in the current procedure, should not be changed.

5.3.4 Influence of baffles

The avoidance of baffles simplifies vessel construction and allows for easier cleaning of the vessel. There is also a reduced power input during agitation. However, large amounts of air are drawn into the emulsion during agitation. This is undesirable for carbonless paper since air can be encapsulated, resulting in wastage of the capsule wall material.

In the laboratory, using baffles greater than 5 mm in width will produce unstable emulsions, i.e. a larger average capsule diameter and a wider size distribution. This is consistent with the theory of "overbaffling." Baffles smaller than 5 mm also gave undesirable results. 5 mm proved to be the best-suited size. Using a tank one-tenth the size of the plant tank, and with triangular baffles resembling the plant, gave acceptable results.

5.4 Surfactants

Different surfactants were tried in order to determine whether there was a more suitable alternative available, than the current one being used. It was not possible to obtain surfactants with similar properties to those of Lupasol. The only available information is that Lupasol is a polyacrylic sulphonic acid derivative, and that its HLB value lies in the range of 14-15, which was determined in the laboratory. Chemical companies that were consulted required more information.

5.5 Particle size analysis

The investigation of the accuracy of Mondi's Malvern Mastersizer has shown that different particle size analysers give different results. The results obtained on a "standard sample" by companies in South Africa were similar to those obtained by Mondi. However, the results obtained by BASF in Germany were very different. When the mode of the Mastersizer presentation was changed according to the BASF procedure, a drastic change was noticed. A unimodal distribution was

observed with less than 1% of small capsules, below 2 microns. The results are discussed in Chapter 4. The use of a linear scale for the diameter should be investigated.

Analyses of the microcapsules by viewing under a microscope showed that the presentation mode used by BASF is probably the correct method. However, this means that only the computer settings must be changed, without changing the method or recipe for microcapsule production. Mondi can still not achieve a six-part carbonless copy set of paper to compete with overseas companies and suggested reasons for this are listed below.

- The concentration and type of solvent, Ruetasolv, used in the ink.
- The type of colourformer dye used to produce the ink.
- The problem could also lie in the CF (Coated Front) side of the paper. More tests should be done on the clay to determine whether better alternatives exist.

5.6 General conclusion and future work

It is concluded that the present operating procedure and type of reagents is optimum and only small improvements were indicated when the impeller speed was reduced for part of the cycle. However, from the evaluation of the microcapsules under a microscope, it is recommended that Mondi change their Mastersizer settings to that of BASF's.

The viscosity of the emulsion should be investigated because it is one of the properties that effect the size distribution of the microcapsules for carbonless copy paper. The viscosity can supply useful information on the rheology of the emulsion, especially when the formic acid is added.

Further investigation on the temperature of the emulsion should be conducted since it is also an important factor, which affects the size distribution of the microcapsules. Investigating temperature, together with an optimum agitator speed could produce a stable, well-dispersed emulsion.

While the estimation of the power drawn by the plant impeller was tentative, it can still be concluded that significant power savings were achieved when the process for emulsion and capsule formation was scaled up. The design of the impeller and ratio of impeller and vessel diameters will need further investigation and an investigation of impeller design may result in improvements in the size distribution of the capsules.

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APPENDIX A

Figures A1 to A6: Typical printouts of the Mastersizer curves

Result: Analysis Table

N 24 O T=30 Run No: 34 Measured: 2/5/2001 11:58
EST1 Rec. No: 442 Analysed: 2/5/2001 11:58
C:\SIZERMUDATA\ Source: Analysed

er: B Measured Beam Obscuration: 21.6 %
ntation: 4OHD Analysis: Polydisperse Residual: 0.675 %
ations: None

= 0.0634 %Vol Density = 1.000 g/cm^3 S.S.A = 0.4307 m^2/g
ution: Volume D[4, 3] = 63.93 um D[3, 2] = 13.93 um
1) = 33.48 um D(v, 0.5) = 62.09 um D(v, 0.9) = 99.93 um
= 1.070E+00 Uniformity = 3.453E-01

Volume In %	Size (um)	Volume In %	Size (um)	Volume In %	Size (um)	Volume In %
0.12	1.95	0.12	12.21	0.00	76.32	12.55
0.23	2.28	0.06	14.22	0.00	88.91	8.82
0.33	2.65	0.02	16.57	0.00	103.58	5.18
0.39	3.09	0.01	19.31	0.00	120.67	2.41
0.43	3.60	0.03	22.49	0.74	140.58	0.68
0.43	4.19	0.08	26.20	1.97	163.77	0.00
0.41	4.88	0.14	30.53	3.73	190.80	0.00
0.37	5.69	0.21	35.56	6.23	222.28	0.00
0.32	6.63	0.27	41.43	9.52	258.95	0.00
0.27	7.72	0.30	48.27	12.84	301.68	
0.22	9.00	0.25	56.23	15.09		
0.17	10.48	0.07	65.51	14.95		
	12.21		76.32			

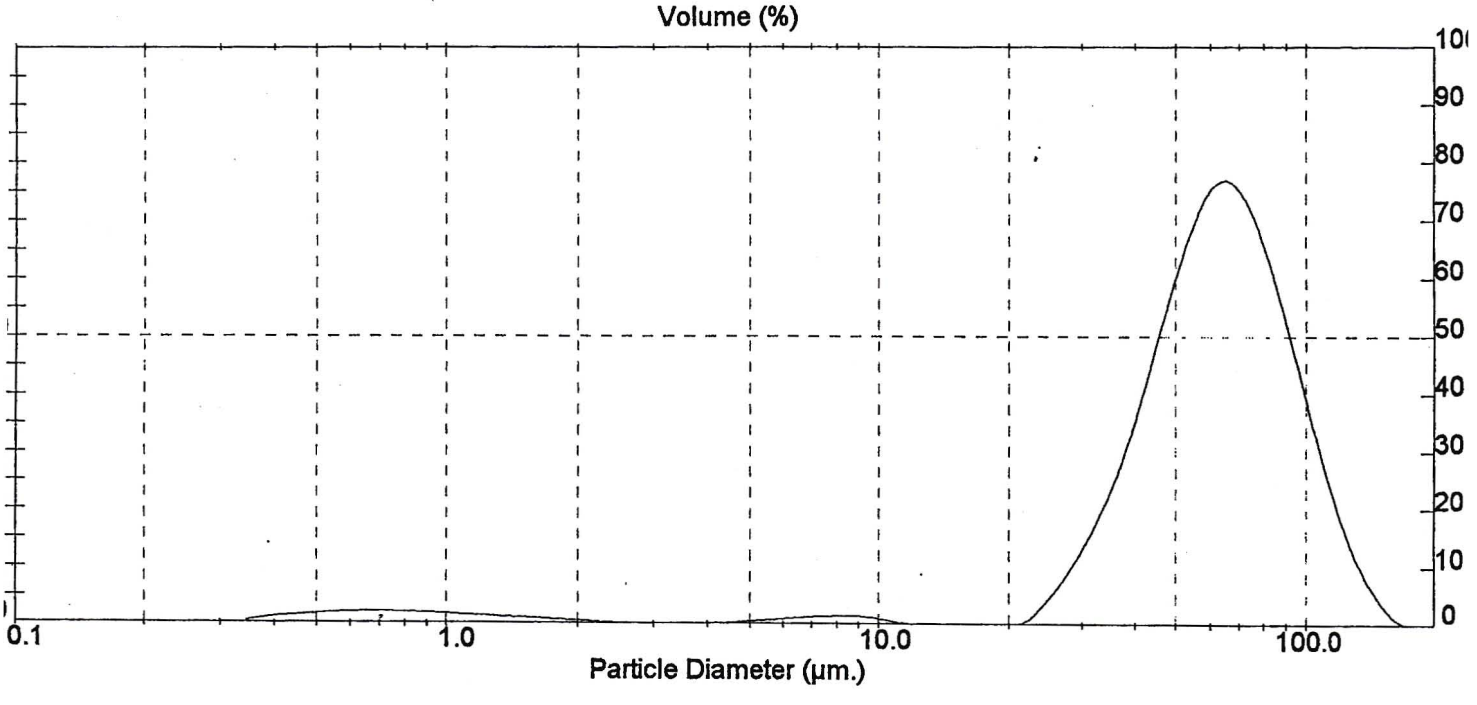

Figure A1: Sample after 10 minutes of emulsification

Result: Analysis Table

24 O T=30	Run No: 35	Measured: 2/5/2001 12:08
ST1	Rec. No: 443	Analysed: 2/5/2001 12:08
\SIZERMUDATA\		Source: Analysed

r: B		Measured Beam Obscuration: 20.3 %
ation: 4OHD	Analysis: Polydisperse	Residual: 0.747 %
itions: None		

0.0416 %Vol	Density = 1.000 g/cm^3	S.S.A. = 0.6050 m^2/g	
tion: Volume	D[4, 3] = 45.22 um	D[3, 2] = 9.92 um	
) = 25.58 um	D(v, 0.5) = 45.62 um	D(v, 0.9) = 66.90 um	
9.058E-01	Uniformity = 2.972E-01		

Volume In %	Size (um)	Volume In %	Size (um)	Volume In %	Size (um)	Volume In %
0.17	1.95	0.14	12.21	0.00	76.32	3.09
0.32	2.28	0.07	14.22	0.00	88.91	0.97
0.45	2.65	0.04	16.57	0.08	103.58	0.09
0.55	3.09	0.06	19.31	0.90	120.67	0.00
0.61	3.60	0.12	22.49	2.21	140.58	0.00
0.63	4.19	0.20	26.20	4.47	163.77	0.00
0.61	4.88	0.28	30.53	8.53	190.80	0.00
0.56	5.69	0.35	35.56	14.52	222.28	0.00
0.50	6.63	0.37	41.43	19.39	258.95	0.00
0.42	7.72	0.24	48.27	18.55	301.68	
0.34	9.00	0.00	56.23	12.92		
0.24	10.48	0.00	65.51	6.97		
	12.21		76.32			

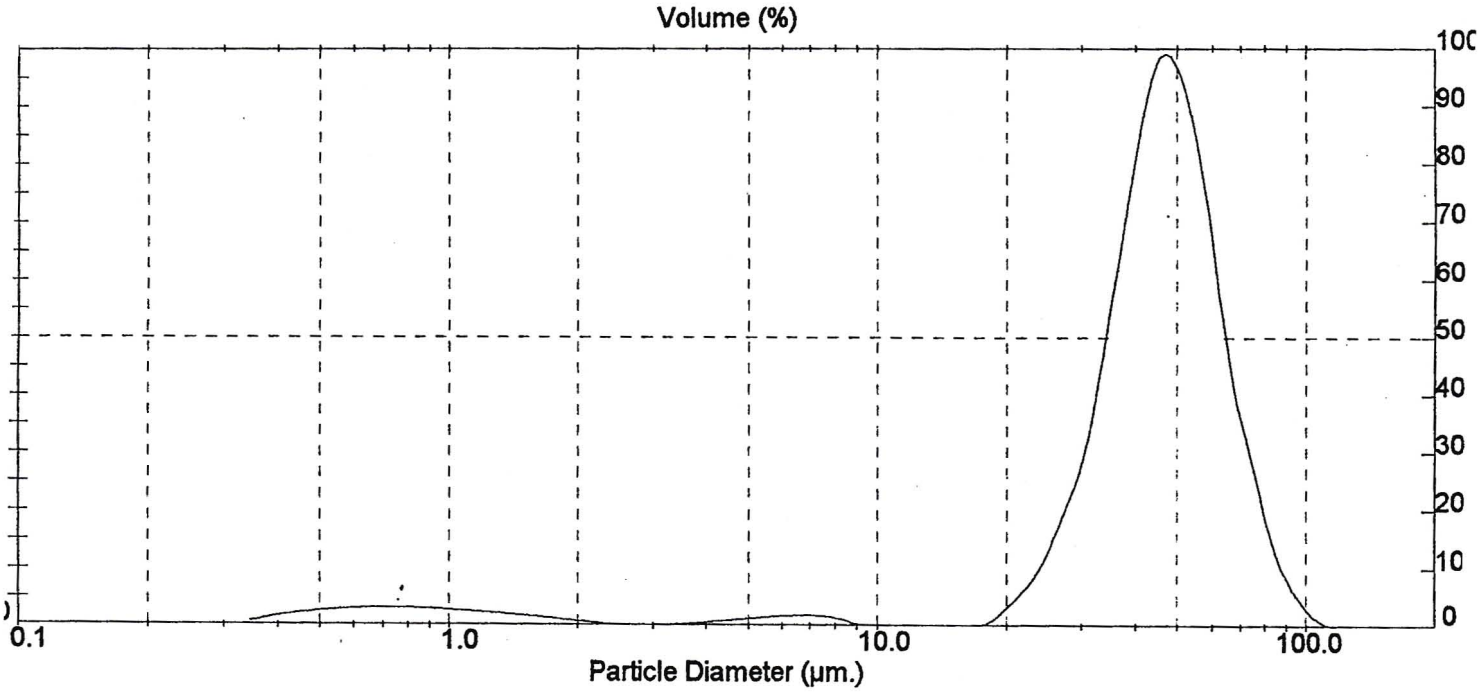

Figure A2: Sample after 20 minutes of emulsification

Result: Analysis Table

N24 O T=30	Run No: 36	Measured: 2/5/2001 12:18
:ST1	Rec. No: 444	Analysed: 2/5/2001 12:18
:\SIZERMU\DATA\		Source: Analysed

ar: B		Measured Beam Obscuration: 20.8 %
itation: 4OHD	Analysis: Polydisperse	Residual: 0.805 %
ations: None		

= 0.0144 %Vol	Density = 1.000 g/cm^3	S.S.A. = 1.7898 m^2/g
ution: Volume	D[4, 3] = 11.22 um	D[3, 2] = 3.35 um
1) = 0.92 um	D(v, 0.5) = 12.11 um	D(v, 0.9) = 17.52 um
= 1.372E+00	Uniformity = 3.606E-01	

Volume In %	Size (um)	Volume In %	Size (um)	Volume In %	Size (um)	Volume In %
0.54	1.95	0.81	12.21	19.04	76.32	0.00
1.03	2.28	0.44	14.22	15.76	88.91	0.00
1.42	2.65	0.00	16.57	9.10	103.58	0.00
1.68	3.09	0.00	19.31	3.82	120.67	0.00
1.80	3.60	0.00	22.49	1.13	140.58	0.00
1.78	4.19	0.00	26.20	0.16	163.77	0.00
1.67	4.88	0.09	30.53	0.00	190.80	0.00
1.49	5.69	0.71	35.56	0.00	222.28	0.00
1.32	6.63	2.19	41.43	0.00	258.95	0.00
1.18	7.72	5.03	48.27	0.00	301.68	
1.09	9.00	9.86	56.23	0.00		
1.00	10.48	15.88	65.51	0.00		
	12.21		76.32			

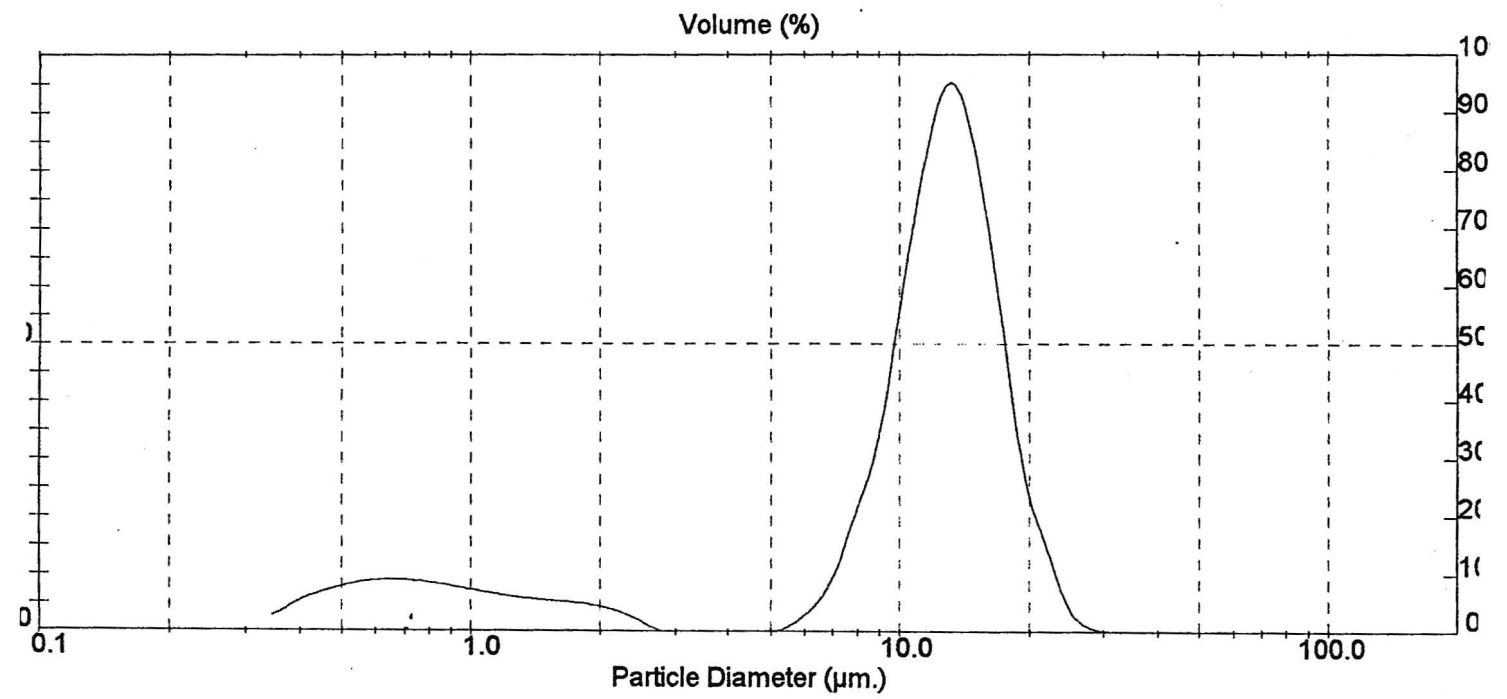

Figure A3: Sample after 30 minutes of emulsification

Result: Analysis Table

RUN 24 O T=30 Run No: 37 Measured: 2/5/2001 12:26
TEST1 Rec. No: 445 Analysed: 2/5/2001 12:26
C:\SIZERMU\DATA\ Source: Analysed

pler: B Measured Beam Obscuration: 21.8 %
entation: 4OHD Analysis: Polydisperse Residual: 2.036 %
ifications: None

c: = 0.0081 %Vol Density = 1.000 g/cm^3 S.S.A.= 3.4001 m^2/g
ibution: Volume D[4, 3] = 4.32 um D[3, 2] = 1.76 um
0.1) = 0.60 um D(v, 0.5) = 4.70 um D(v, 0.9) = 7.63 um
n = 1.497E+00 Uniformity = 4.767E-01

e)	Volume In %	Size (um)	Volume In %	Size (um)	Volume In %	Size (um)	Volume In %
31	1.06	1.95	0.25	12.21	0.07	76.32	0.00
36	2.01	2.28	0.61	14.22	0.00	88.91	0.00
42	2.77	2.65	1.60	16.57	0.00	103.58	0.00
49	3.30	3.09	3.68	19.31	0.00	120.67	0.00
58	3.58	3.60	6.95	22.49	0.00	140.58	0.00
67	3.61	4.19	10.80	26.20	0.00	163.77	0.00
78	3.40	4.88	13.59	30.53	0.00	190.80	0.00
91	3.00	5.69	13.56	35.56	0.00	222.28	0.00
06	2.46	6.63	10.40	41.43	0.00	258.95	0.00
24	1.85	7.72	6.02	48.27	0.00	301.68	
44	1.28	9.00	2.56	56.23	0.00		
68	0.89	10.48	0.71	65.51	0.00		
95		12.21		76.32			

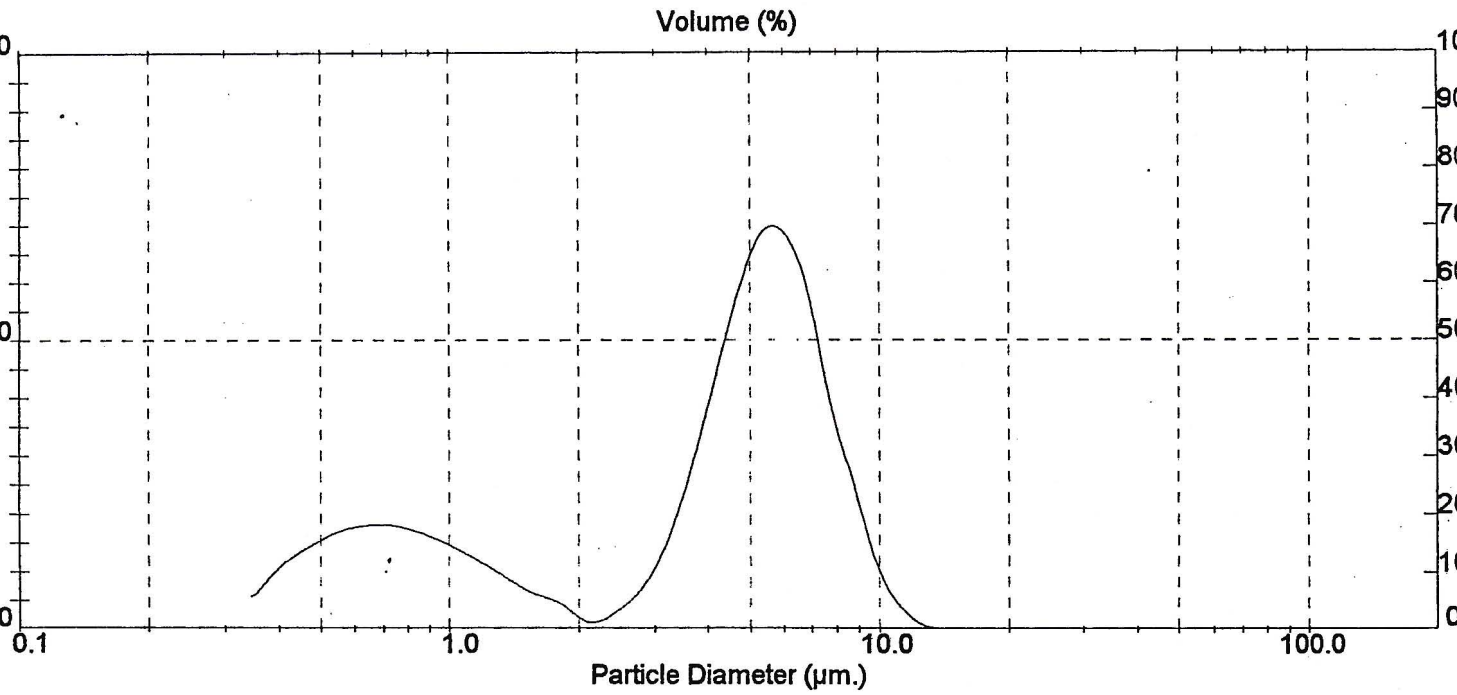

Figure A4: Sample after 40 minutes of emulsification

Result: Analysis Table

24 O T=30	Run No.: 38	Measured: 2/5/2001 12:33
3T1	Rec. No: 446	Analysed: 2/5/2001 12:33
\SIZERMU\DATA\		Source: Analysed

r B		Measured Beam Obscuration: 19.8 %
ation: 4OHD	Analysis: Polydisperse	Residual: 1.575 %
itions: None		

0.0050 %Vol	Density = 1.000 g/cm^3	S.S.A. = 5.7064 m^2/g
tion: Volume	D[4, 3] = 2.37 um	D[3, 2] = 1.05 um
) = 0.45 um	D(v, 0.5) = 2.52 um	D(v, 0.9) = 4.70 um
1.687E+00	Uniformity = 6.267E-01	

Volume In %	Size (um)	Volume In %	Size (um)	Volume In %	Size (um)	Volume In %
2.78	1.95	1.68	12.21	0.00	76.32	0.00
5.01	2.28	4.31	14.22	0.00	88.91	0.00
6.51	2.65	8.09	16.57	0.00	103.58	0.00
7.18	3.09	11.26	19.31	0.00	120.67	0.00
7.02	3.60	11.69	22.49	0.00	140.58	0.00
6.15	4.19	9.10	26.20	0.00	163.77	0.00
4.78	4.88	5.24	30.53	0.00	190.80	0.00
3.21	5.69	2.18	35.56	0.00	222.28	0.00
1.78	6.63	0.57	41.43	0.00	258.95	0.00
0.81	7.72	0.05	48.27	0.00	301.68	
0.13	9.00	0.00	56.23	0.00		
0.47	10.48	0.00	65.51	0.00		
	12.21		76.32			

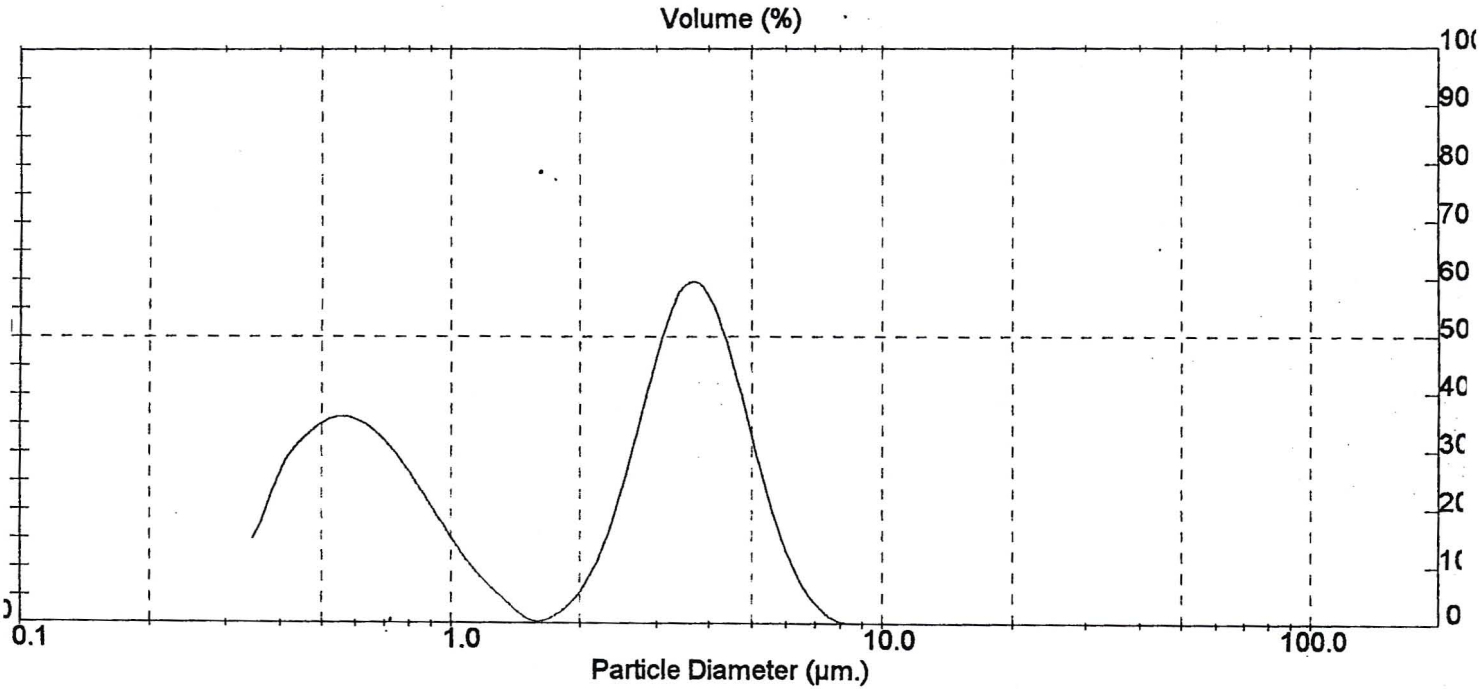

Figure A5: Sample after 50 minutes of emulsification

Result: Analysis Table

4 24 O T=30	Run No: 39	Measured: 2/5/2001 12:41	
:STT	Rec. No: 447	Analysed: 2/5/2001 12:41	
:\SIZERMU\DATA\		Source: Analysed	
r: B		Measured Beam Obscuration: 23.6 %	
lation: 4OHD	Analysis: Polydisperse	Residual: 2.603 %	
ations: None			
= 0.0051 %Vol	Density = 1.000 g/cm^3	S.S.A. = 6.0033 m^2/g	
ition: Volume	D[4, 3] = 1.67 um	D[3, 2] = 1.00 um	
f) = 0.49 um	D(v, 0.5) = 1.28 um	D(v, 0.9) = 3.40 um	
2.267E+00	Uniformity = 7.438E-01		

Volume In %	Size (um)	Volume In %	Size (um)	Volume In %	Size (um)	Volume In %
1.52	1.95	6.90	12.21	0.00	76.32	0.00
3.56	2.28	7.59	14.22	0.00	88.91	0.00
5.44	2.65	7.36	16.57	0.00	103.58	0.00
6.78	3.09	6.15	19.31	0.00	120.67	0.00
7.37	3.60	4.32	22.49	0.00	140.58	0.00
7.22	4.19	2.44	26.20	0.00	163.77	0.00
6.52	4.88	0.98	30.53	0.00	190.80	0.00
5.60	5.69	0.16	35.56	0.00	222.28	0.00
4.85	6.63	0.00	41.43	0.00	258.95	0.00
4.57	7.72	0.00	48.27	0.00	301.68	
4.91	9.00	0.00	56.23	0.00		
5.80	10.48	0.00	65.51	0.00		
	12.21		76.32			

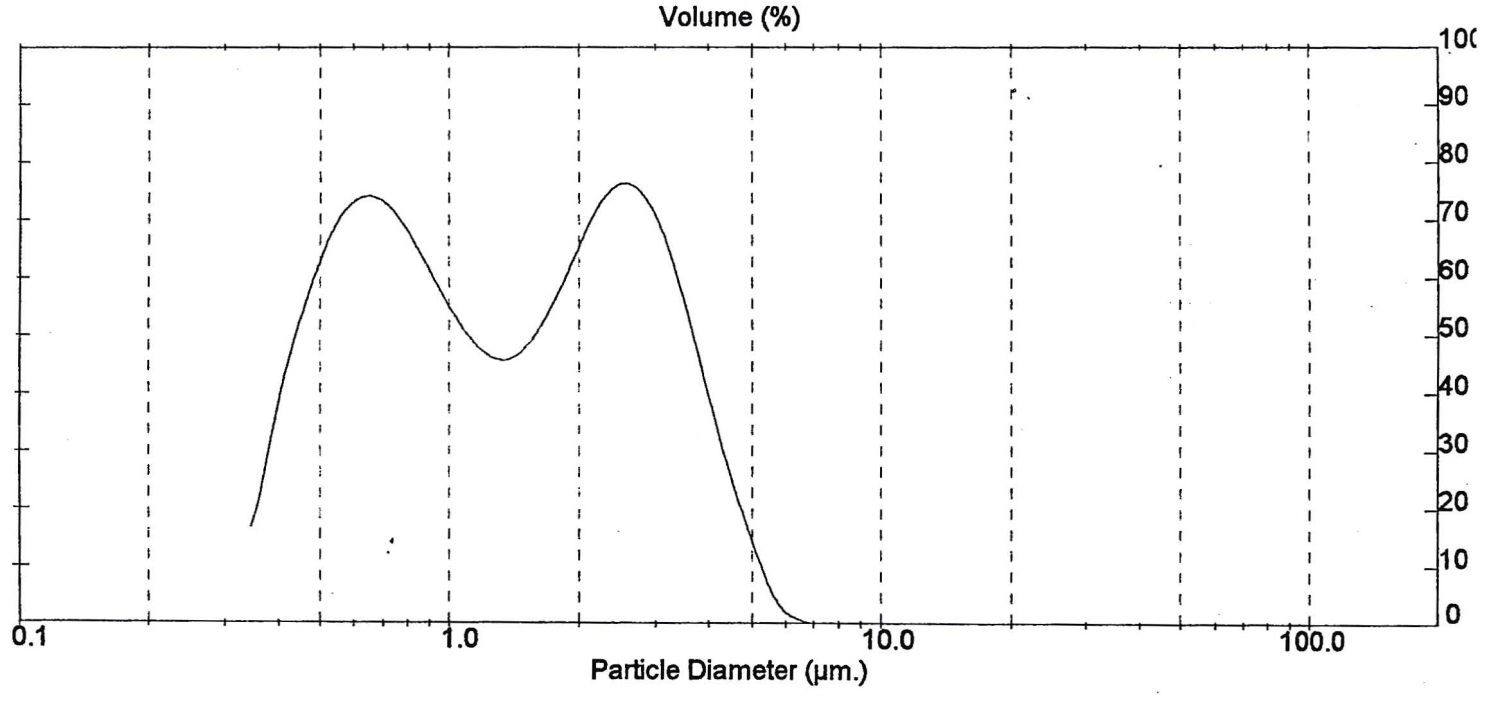

Figure A6: Sample after 60 minutes of emulsification

APPENDIX B

Figure B1: Plant impeller speeds

Calculation of impeller tip speeds

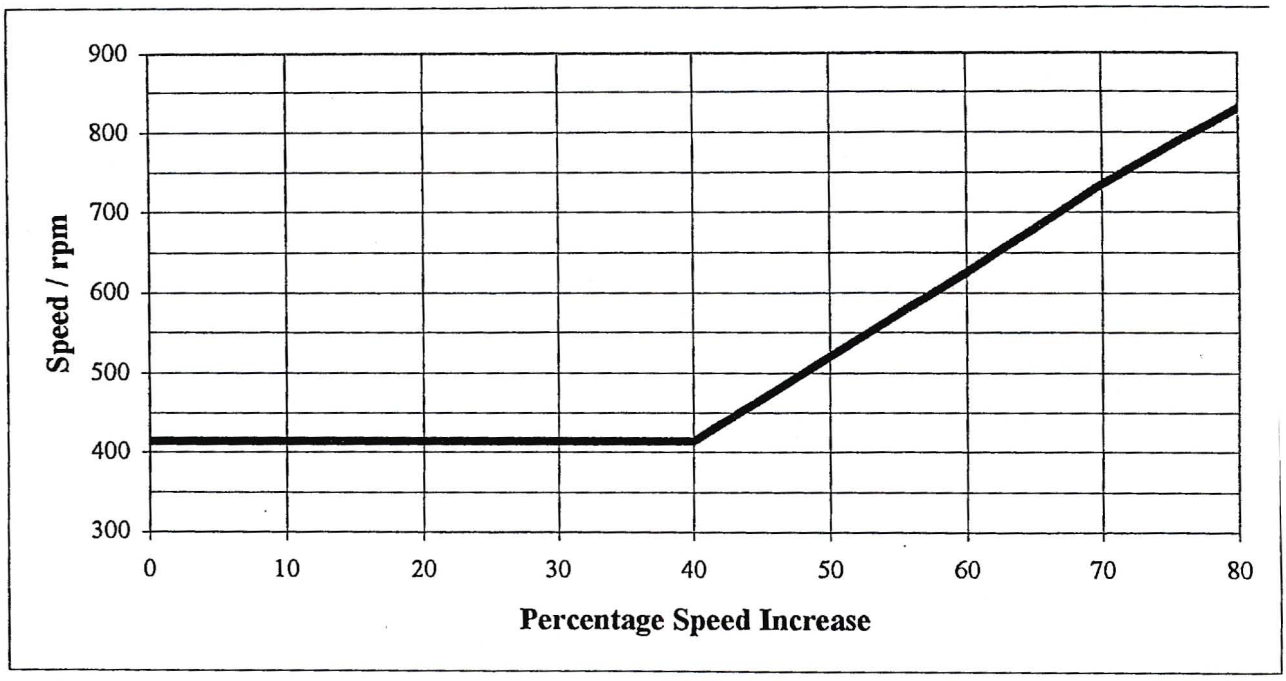

Figure B1: Plant agitator speeds

Calculation of the impeller tip speeds

$$\frac{\text{Laboratory agitation speed (rpm)}}{60} \times \pi D = \text{impeller tip speed (m/s)}, \quad (1)$$

where D is the diameter of the laboratory impeller, 0.045 m.

Therefore, $7500 \text{ rpm} \times \pi(0.045) = 18 \text{ m/s}.$

Similarly, 7200 rpm corresponds to 17 m/s. Therefore, a reduction in operating speed from 7500 rpm to 7200 rpm corresponds to a reduction of 1 m/s in impeller tip speed. The plant impeller tip speed was worked out in the same manner:

$$\frac{\text{Plant agitation speed (rpm)}}{60} \times \pi d = \text{impeller tip speed (m/s)}, \quad (2)$$

where d is the diameter of the plant impeller, 0.540 m. The emulsification process, i.e. after the addition of formic acid at the plant, was done at an impeller speed of 75%. According to Figure B.1, this corresponds to approximately 775 rpm.

Therefore, $775 \text{ rpm} \times \pi (0.540) = 22 \text{ m/s}.$

A decrease in 1 m/s, from 22 to 21 m/s, worked out to be 735 rpm, using Equation 2. According to Figure B1, this corresponds to 70% agitation speed of the plant impeller.

APPENDIX C

Figures C1 to C8: Comparison between Mondi and BASF presentation modes

Result: Analysis Report

Sample Details

Sample ID: RUN 3B - T=30
Sample File: TEST1
Sample Path: C:\SIZERMU\DATA\
Sample Notes: NEW SCALE-DOWN TANK
7500 RPM...20 MIN
7200 RPM...20 MIN
SAMPLE 1 - 10 MIN AFTER ACID ADDITION

Run Number: 1
Record Number: 1099

Measured: 10 Jan 2002 11:20
Analysed: 10 Jan 2002 11:20
Result Source: Analysed

System Details

Sampler: B
Presentation: 4OHD
Analysis Model: Polydisperse
Modifications: None

[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Measured Beam Obscuration: 20.2 %

Residual: 1.192 %

Result Statistics

Distribution Type: Volume
Mean Diameters:
D [4, 3] = 66.43 um

Concentration = 0.0716 %Vol
D (v, 0.1) = 40.87 um
D [3, 2] = 17.35 um

Density = 1.000 g / cub. cm
D (v, 0.5) = 65.86 um
Span = 8.285E-01

Specific S.A. = 0.3458 sq. m / g
D (v, 0.9) = 95.43 um
Uniformity = 2.761E-01

Size Low (um)	In %	Size High (um)	Under%	Size Low (um)	In %	Size High (um)	Under%
0.31	0.09	0.36	0.09	10.48	0.22	12.21	4.12
0.36	0.18	0.42	0.28	12.21	0.00	14.22	4.12
0.42	0.25	0.49	0.53	14.22	0.00	16.57	4.12
0.49	0.30	0.58	0.83	16.57	0.00	19.31	4.12
0.58	0.33	0.67	1.16	19.31	0.00	22.49	4.12
0.67	0.33	0.78	1.49	22.49	0.00	26.20	4.12
0.78	0.31	0.91	1.80	26.20	0.58	30.53	4.69
0.91	0.28	1.06	2.08	30.53	1.84	35.56	6.54
1.06	0.24	1.24	2.33	35.56	3.94	41.43	10.48
1.24	0.21	1.44	2.53	41.43	7.52	48.27	18.01
1.44	0.17	1.68	2.71	48.27	12.85	56.23	30.86
1.68	0.13	1.95	2.84	56.23	18.43	65.51	49.30
1.95	0.08	2.28	2.93	65.51	19.88	76.32	69.17
2.28	0.03	2.65	2.95	76.32	15.67	88.91	84.84
2.65	0.00	3.09	2.95	88.91	9.25	103.58	94.09
3.09	0.00	3.60	2.95	103.58	4.30	120.67	98.39
3.60	0.00	4.19	2.95	120.67	1.46	140.58	99.85
4.19	0.00	4.88	2.95	140.58	0.15	163.77	100.00
4.88	0.05	5.69	3.00	163.77	0.00	190.80	100.00
5.69	0.13	6.63	3.13	190.80	0.00	222.28	100.00
6.63	0.20	7.72	3.33	222.28	0.00	258.95	100.00
7.72	0.27	9.00	3.60	258.95	0.00	301.68	100.00
9.00	0.30	10.48	3.90				

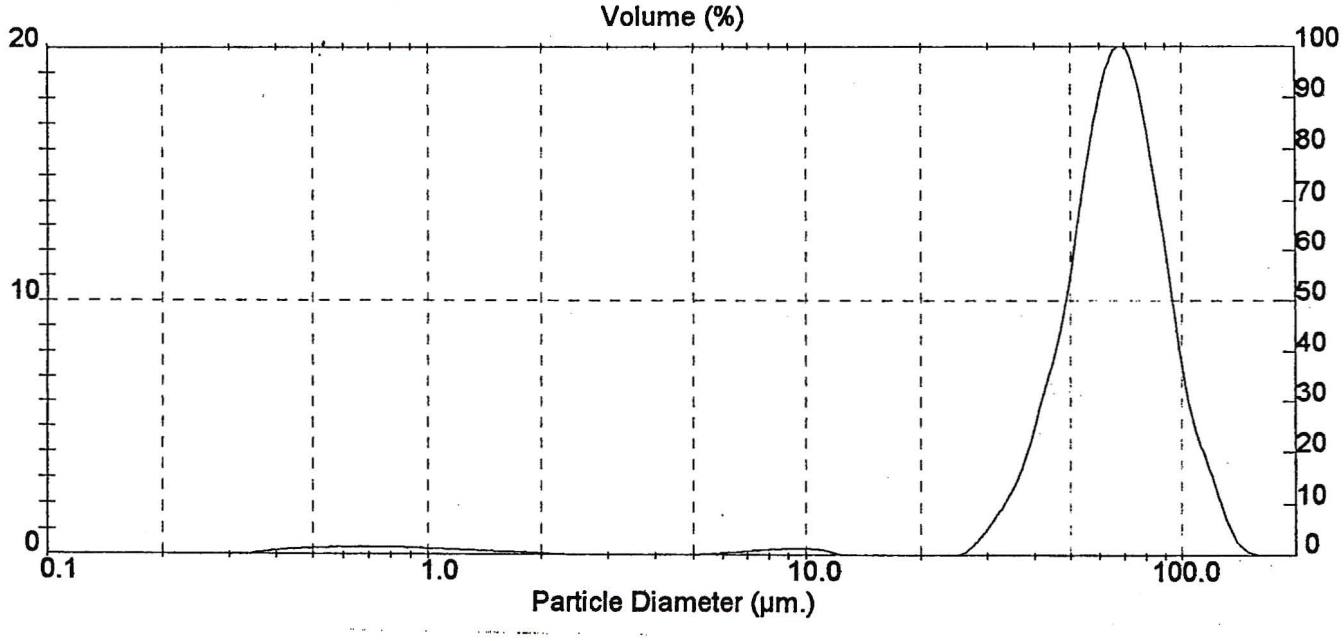

Figure C1: Mondi presentation mode – 10 minutes after emulsification

Result: Analysis Report

Sample Details

Sample ID: RUN 3B - T=30
Sample File: (Result Not Saved)
Sample Path: C:\SIZERMU\DATA\
Sample Notes: NEW SCALE-DOWN TANK
7500 RPM...20 MIN
7200 RPM...20 MIN
SAMPLE 1 - 10 MIN AFTER ACID ADDITION

Run Number: 6

Measured: 10 Jan 2002 11:20
Analysed: 10 Jan 2002 11:51
Result Source: Analysed

System Details

Sampler: B
Presentation: 4OAD
Analysis Model: Polydisperse
Modifications: None

[Particle R.I. = (1.5295, 0.0000); Dispersant R.I. = 1.3300]

Measured Beam Obscuration: 20.2 %

Residual: 1.207 %

Result Statistics

Distribution Type: Volume
Mean Diameters:
D [4, 3] = 68.40 um

Concentration = 0.1782 %Vol
D (v, 0.1) = 43.54 um
D [3, 2] = 57.79 um

Density = 1.000 g / cub. cm
D (v, 0.5) = 66.57 um
Span = 7.975E-01

Specific S.A. = 0.1038 sq. m / g
D (v, 0.9) = 96.62 um
Uniformity = 2.527E-01

Size Low (um)	In %	Size High (um)	Under%	Size Low (um)	In %	Size High (um)	Under%
0.31	0.00	0.36	0.00	10.48	0.14	12.21	1.30
0.36	0.00	0.42	0.00	12.21	0.00	14.22	1.30
0.42	0.00	0.49	0.00	14.22	0.00	16.57	1.30
0.49	0.00	0.58	0.00	16.57	0.00	19.31	1.30
0.58	0.00	0.67	0.00	19.31	0.00	22.49	1.30
0.67	0.00	0.78	0.00	22.49	0.00	26.20	1.30
0.78	0.00	0.91	0.00	26.20	0.56	30.53	1.86
0.91	0.00	1.06	0.00	30.53	1.87	35.56	3.73
1.06	0.00	1.24	0.00	35.56	4.10	41.43	7.83
1.24	0.00	1.44	0.00	41.43	7.82	48.27	15.65
1.44	0.00	1.68	0.00	48.27	13.23	56.23	28.88
1.68	0.00	1.95	0.00	56.23	18.95	65.51	47.83
1.95	0.00	2.28	0.00	65.51	20.38	76.32	68.21
2.28	0.00	2.65	0.00	76.32	16.10	88.91	84.31
2.65	0.00	3.09	0.00	88.91	9.53	103.58	93.84
3.09	0.00	3.60	0.00	103.58	4.46	120.67	98.29
3.60	0.00	4.19	0.00	120.67	1.54	140.58	99.83
4.19	0.04	4.88	0.04	140.58	0.17	163.77	100.00
4.88	0.10	5.69	0.14	163.77	0.00	190.80	100.00
5.69	0.17	6.63	0.31	190.80	0.00	222.28	100.00
6.63	0.28	7.72	0.59	222.28	0.00	258.95	100.00
7.72	0.27	9.00	0.86	258.95	0.00	301.68	100.00
9.00	0.30	10.48	1.16				

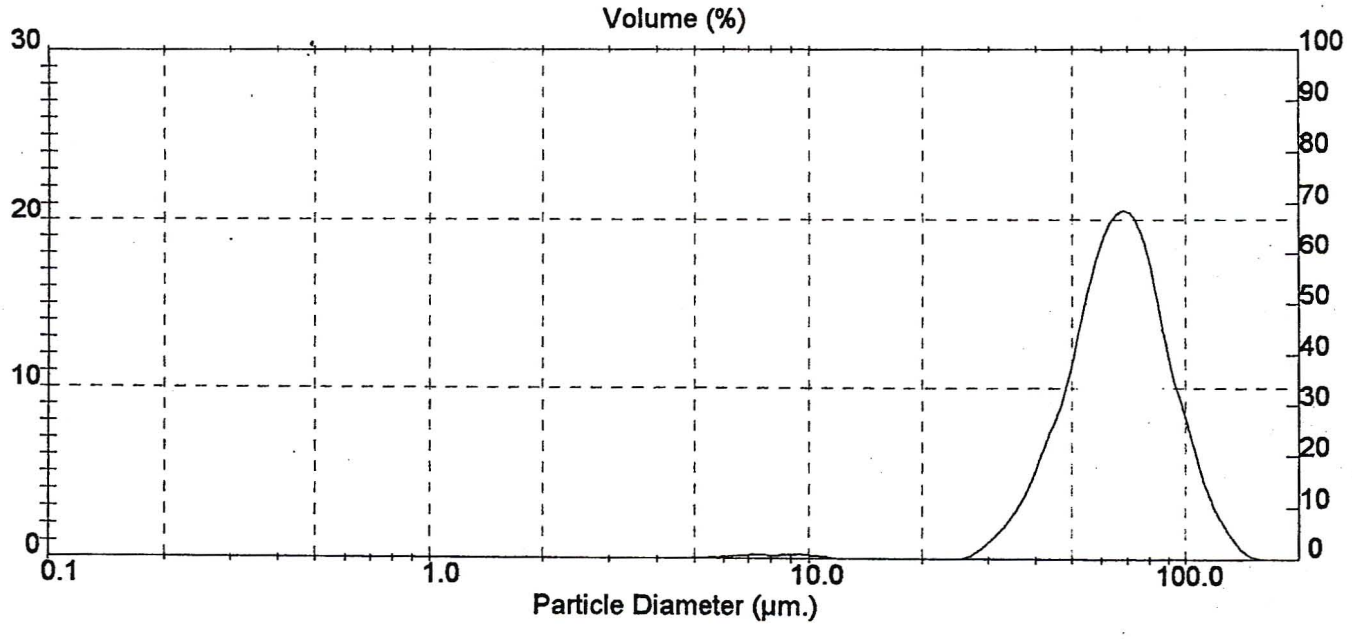

Figure C2: BASF presentation mode – 10 minutes after emulsification

Result: Analysis Report

Sample Details

Sample ID: RUN 3B - T=30
Sample File: TEST1
Sample Path: C:\SIZERMU\DATA\
Sample Notes: NEW SCALE-DOWN TANK
7500 RPM...20 MIN
7200 RPM...20 MIN
SAMPLE 2 - 20 MIN AFTER ACID ADDITION

Run Number: 2
Record Number: 1100

Measured: 10 Jan 2002 11:31
Analysed: 10 Jan 2002 11:31
Result Source: Analysed

System Details

Sampler: B
Presentation: 4OHD
Analysis Model: Polydisperse
Modifications: None

[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Measured Beam Obscuration: 32.0 %

Residual: 0.508 %

Result Statistics

Distribution Type: Volume
Mean Diameters:
D [4, 3] = 10.71 um

Concentration = 0.0251 %Vol
D (v, 0.1) = 1.01 um
D [3, 2] = 3.54 um

Density = 1.000 g / cub. cm
D (v, 0.5) = 11.23 um
Span = 1.413E+00

Specific S.A. = 1.6963 sq. m / g
D (v, 0.9) = 16.87 um
Uniformity = 3.580E-01

Size Low (um)	In %	Size High (um)	Under%	Size Low (um)	In %	Size High (um)	Under%
0.31	0.51	0.36	0.51	10.48	17.11	12.21	59.66
0.36	0.97	0.42	1.48	12.21	17.07	14.22	76.73
0.42	1.32	0.49	2.80	14.22	12.35	16.57	89.07
0.49	1.56	0.58	4.36	16.57	6.82	19.31	95.89
0.58	1.65	0.67	6.01	19.31	3.00	22.49	98.89
0.67	1.62	0.78	7.63	22.49	0.97	26.20	99.87
0.78	1.49	0.91	9.12	26.20	0.13	30.53	100.00
0.91	1.31	1.06	10.43	30.53	0.00	35.56	100.00
1.06	1.13	1.24	11.56	35.56	0.00	41.43	100.00
1.24	0.99	1.44	12.55	41.43	0.00	48.27	100.00
1.44	0.89	1.68	13.44	48.27	0.00	56.23	100.00
1.68	0.75	1.95	14.19	56.23	0.00	65.51	100.00
1.95	0.45	2.28	14.65	65.51	0.00	76.32	100.00
2.28	0.00	2.65	14.65	76.32	0.00	88.91	100.00
2.65	0.00	3.09	14.65	88.91	0.00	103.58	100.00
3.09	0.00	3.60	14.65	103.58	0.00	120.67	100.00
3.60	0.00	4.19	14.65	120.67	0.00	140.58	100.00
4.19	0.10	4.88	14.74	140.58	0.00	163.77	100.00
4.88	0.81	5.69	15.55	163.77	0.00	190.80	100.00
5.69	2.12	6.63	17.67	190.80	0.00	222.28	100.00
6.63	4.29	7.72	21.96	222.28	0.00	258.95	100.00
7.72	7.81	9.00	29.77	258.95	0.00	301.68	100.00
9.00	12.78	10.48	42.55				

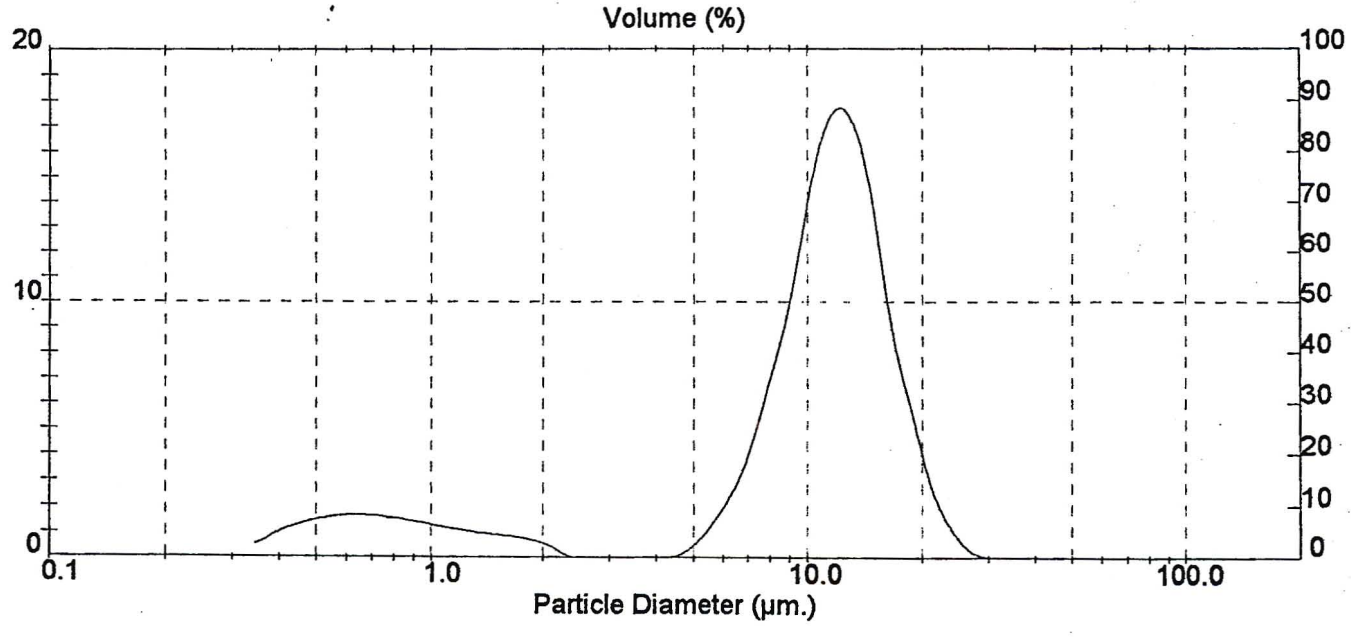

Figure C3: Mondi presentation mode – 20 minutes after emulsification

Result: Analysis Report

Sample Details

Sample ID: RUN 3B - T=30
Sample File: (Result Not Saved)
Sample Path: C:\SIZERMU\DATA\
Sample Notes: NEW SCALE-DOWN TANK
7500 RPM...20 MIN
7200 RPM...20 MIN
SAMPLE 2 - 20 MIN AFTER ACID ADDITION

Run Number: 7

Measured: 10 Jan 2002 11:31
Analysed: 10 Jan 2002 11:53
Result Source: Analysed

System Details

Sampler: B
Presentation: 4OAD
Analysis Model: Polydisperse
Modifications: None

[Particle R.I. = (1.5295, 0.0000); Dispersant R.I. = 1.3300]

Measured Beam Obscuration: 32.0 %

Residual: 0.506 %

Result Statistics

Distribution Type: Volume
Mean Diameters:
D [4, 3] = 11.93 um

Concentration = 0.0464 %Vol
D (v, 0.1) = 7.34 um
D [3, 2] = 7.87 um

Density = 1.000 g / cub. cm
D (v, 0.5) = 11.66 um
Span = 8.399E-01

Specific S.A. = 0.7624 sq. m / g
D (v, 0.9) = 17.14 um
Uniformity = 2.734E-01

Size Low (um)	In %	Size High (um)	Under%	Size Low (um)	In %	Size High (um)	Under%
0.31	0.02	0.36	0.02	10.48	18.91	12.21	55.70
0.36	0.08	0.42	0.09	12.21	18.25	14.22	73.94
0.42	0.16	0.49	0.25	14.22	13.80	16.57	87.74
0.49	0.26	0.58	0.51	16.57	7.78	19.31	95.52
0.58	0.36	0.67	0.87	19.31	3.26	22.49	98.78
0.67	0.44	0.78	1.31	22.49	1.05	26.20	99.83
0.78	0.49	0.91	1.80	26.20	0.17	30.53	100.00
0.91	0.48	1.06	2.28	30.53	0.00	35.56	100.00
1.06	0.43	1.24	2.71	35.56	0.00	41.43	100.00
1.24	0.33	1.44	3.04	41.43	0.00	48.27	100.00
1.44	0.17	1.68	3.21	48.27	0.00	56.23	100.00
1.68	0.00	1.95	3.21	56.23	0.00	65.51	100.00
1.95	0.00	2.28	3.21	65.51	0.00	76.32	100.00
2.28	0.00	2.65	3.21	76.32	0.00	88.91	100.00
2.65	0.00	3.09	3.21	88.91	0.00	103.58	100.00
3.09	0.00	3.60	3.21	103.58	0.00	120.67	100.00
3.60	0.00	4.19	3.21	120.67	0.00	140.58	100.00
4.19	0.21	4.88	3.42	140.58	0.00	163.77	100.00
4.88	0.85	5.69	4.27	163.77	0.00	190.80	100.00
5.69	2.32	6.63	6.59	190.80	0.00	222.28	100.00
6.63	5.60	7.72	12.19	222.28	0.00	258.95	100.00
7.72	8.51	9.00	20.70	258.95	0.00	301.68	100.00
9.00	16.08	10.48	36.78				

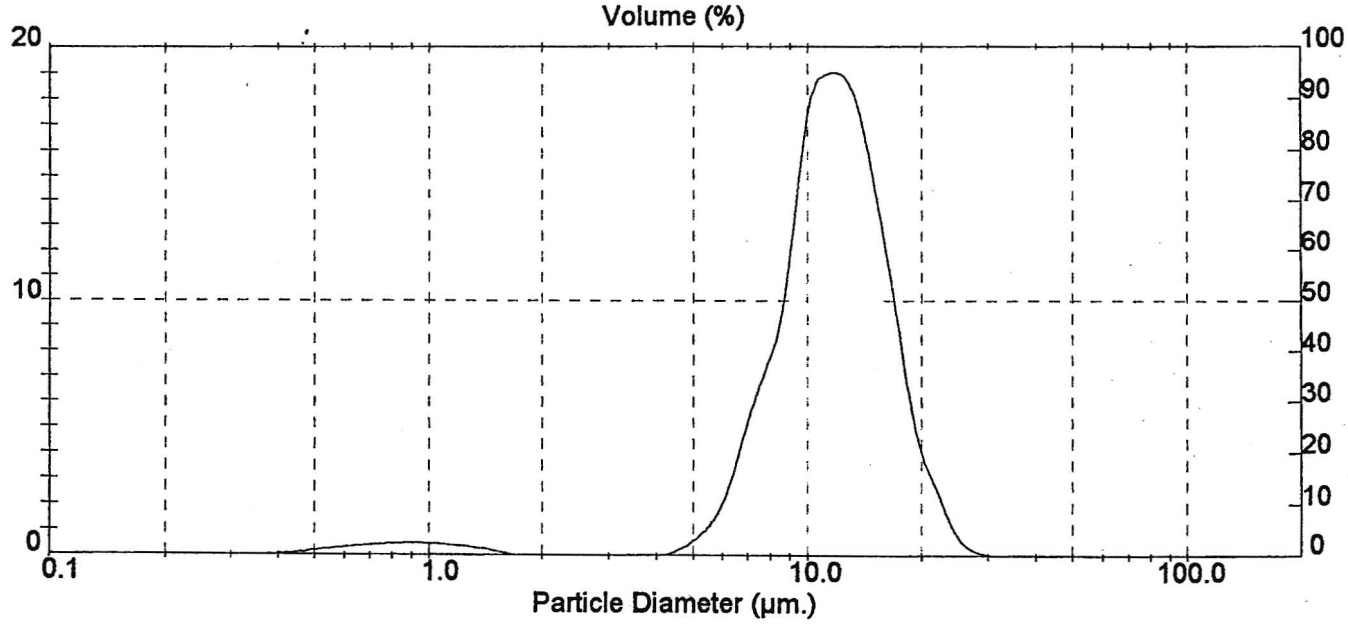

Figure C4: BASF presentation mode – 20 minutes after emulsification

Result: Analysis Report

Sample Details

Sample ID: RUN 3B - T=30
Sample File: TEST1
Sample Path: C:\SIZERMU\DATA\
Sample Notes: NEW SCALE-DOWN TANK
7500 RPM...20 MIN
7200 RPM...20 MIN
SAMPLE 3 - 30 MIN AFTER ACID ADDITION

Run Number: 3
Record Number: 1101

Measured: 10 Jan 2002 11:38
Analysed: 10 Jan 2002 11:38
Result Source: Analysed

System Details

Sampler: B
Presentation: 4OHD
Analysis Model: Polydisperse
Modifications: None

[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Measured Beam Obscuration: 22.3 %

Residual: 0.536 %

Result Statistics

Distribution Type: Volume
Mean Diameters:
D [4, 3] = 4.95 um

Concentration = 0.0098 %Vol
D (v, 0.1) = 0.67 um
D [3, 2] = 2.13 um

Density = 1.000 g / cub. cm
D (v, 0.5) = 5.19 um
Span = 1.487E+00

Specific S.A. = 2.8153 sq. m / g
D (v, 0.9) = 8.38 um
Uniformity = 4.266E-01

Size Low (um)	In %	Size High (um)	Under%	Size Low (um)	In %	Size High (um)	Under%
0.31	0.82	0.36	0.82	10.48	1.82	12.21	99.52
0.36	1.57	0.42	2.38	12.21	0.48	14.22	100.00
0.42	2.19	0.49	4.57	14.22	0.00	16.57	100.00
0.49	2.62	0.58	7.19	16.57	0.00	19.31	100.00
0.58	2.84	0.67	10.03	19.31	0.00	22.49	100.00
0.67	2.83	0.78	12.86	22.49	0.00	26.20	100.00
0.78	2.59	0.91	15.45	26.20	0.00	30.53	100.00
0.91	2.15	1.06	17.60	30.53	0.00	35.56	100.00
1.06	1.58	1.24	19.18	35.56	0.00	41.43	100.00
1.24	0.97	1.44	20.14	41.43	0.00	48.27	100.00
1.44	0.46	1.68	20.60	48.27	0.00	56.23	100.00
1.68	0.09	1.95	20.69	56.23	0.00	65.51	100.00
1.95	0.26	2.28	20.95	65.51	0.00	76.32	100.00
2.28	0.81	2.65	21.76	76.32	0.00	88.91	100.00
2.65	1.92	3.09	23.68	88.91	0.00	103.58	100.00
3.09	3.86	3.60	27.53	103.58	0.00	120.67	100.00
3.60	6.77	4.19	34.31	120.67	0.00	140.58	100.00
4.19	10.51	4.88	44.82	140.58	0.00	163.77	100.00
4.88	13.73	5.69	58.55	163.77	0.00	190.80	100.00
5.69	14.58	6.63	73.13	190.80	0.00	222.28	100.00
6.63	12.15	7.72	85.28	222.28	0.00	258.95	100.00
7.72	8.08	9.00	93.35	258.95	0.00	301.68	100.00
9.00	4.35	10.48	97.70				

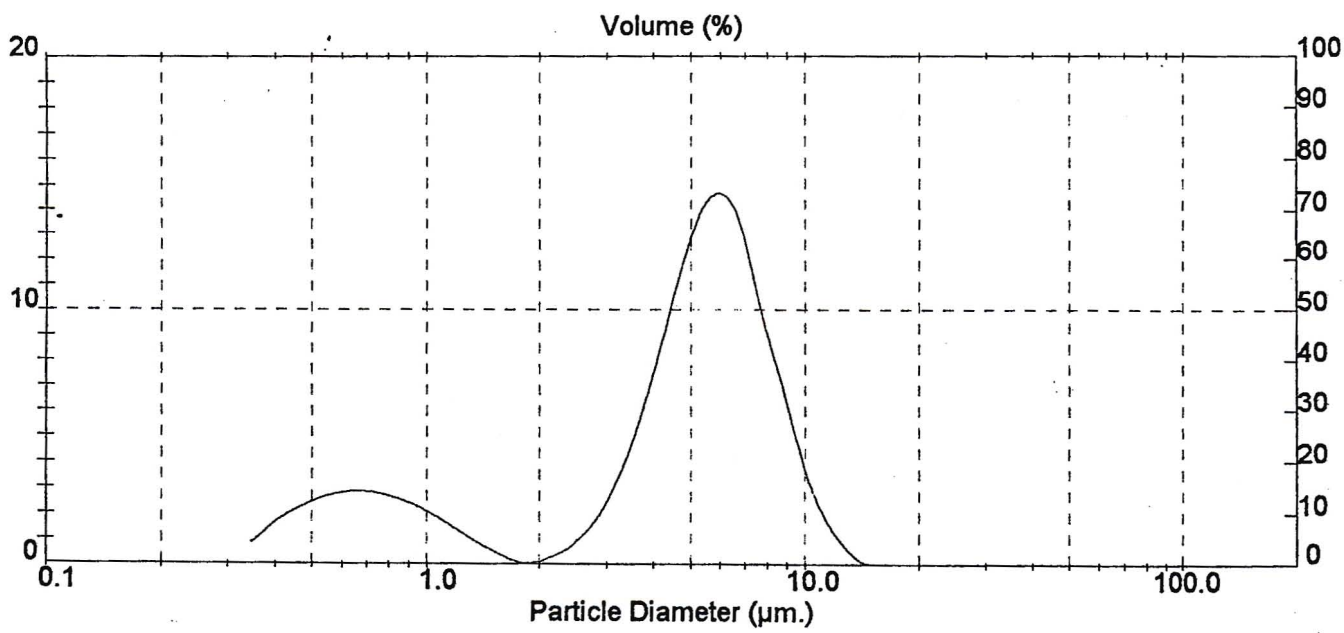

Figure C5: Mondi presentation mode – 30 minutes after emulsification

Result: Analysis Report

Sample Details

Sample ID: RUN 3B - T=30
Sample File: (Result Not Saved)
Sample Path: C:\SIZERMU\DATA\
Sample Notes: NEW SCALE-DOWN TANK
7500 RPM...20 MIN
7200 RPM...20 MIN
SAMPLE 3 - 30 MIN AFTER ACID ADDITION

Run Number: 8

Measured: 10 Jan 2002 11:38
Analysed: 10 Jan 2002 11:55
Result Source: Analysed

System Details

Sampler: B
Presentation: 4OAD
Analysis Model: Polydisperse
Modifications: None

[Particle R.I. = (1.5295, 0.0000); Dispersant R.I. = 1.3300]

Measured Beam Obscuration: 22.3 %

Residual: 0.622 %

Result Statistics

Distribution Type: Volume
Mean Diameters:
D [4, 3] = 6.01 um

Concentration = 0.0168 %Vol
D (v, 0.1) = 3.53 um
D [3, 2] = 5.29 um

Density = 1.000 g / cub. cm
D (v, 0.5) = 5.70 um
Span = 9.408E-01

Specific S.A. = 1.1346 sq. m / g
D (v, 0.9) = 8.89 um
Uniformity = 3.001E-01

Size Low (um)	In %	Size High (um)	Under%	Size Low (um)	In %	Size High (um)	Under%
0.31	0.00	0.36	0.00	10.48	2.94	12.21	98.92
0.36	0.00	0.42	0.00	12.21	0.94	14.22	99.86
0.42	0.00	0.49	0.00	14.22	0.14	16.57	100.00
0.49	0.00	0.58	0.00	16.57	0.00	19.31	100.00
0.58	0.00	0.67	0.00	19.31	0.00	22.49	100.00
0.67	0.00	0.78	0.00	22.49	0.00	26.20	100.00
0.78	0.00	0.91	0.00	26.20	0.00	30.53	100.00
0.91	0.00	1.06	0.00	30.53	0.00	35.56	100.00
1.06	0.00	1.24	0.00	35.56	0.00	41.43	100.00
1.24	0.00	1.44	0.00	41.43	0.00	48.27	100.00
1.44	0.00	1.68	0.00	48.27	0.00	56.23	100.00
1.68	0.01	1.95	0.01	56.23	0.00	65.51	100.00
1.95	0.40	2.28	0.41	65.51	0.00	76.32	100.00
2.28	1.32	2.65	1.73	76.32	0.00	88.91	100.00
2.65	2.93	3.09	4.66	88.91	0.00	103.58	100.00
3.09	6.38	3.60	11.04	103.58	0.00	120.67	100.00
3.60	10.60	4.19	21.64	120.67	0.00	140.58	100.00
4.19	12.40	4.88	34.04	140.58	0.00	163.77	100.00
4.88	15.84	5.69	49.88	163.77	0.00	190.80	100.00
5.69	17.03	6.63	66.91	190.80	0.00	222.28	100.00
6.63	12.79	7.72	79.70	222.28	0.00	258.95	100.00
7.72	11.01	9.00	90.71	258.95	0.00	301.68	100.00
9.00	5.27	10.48	95.98				

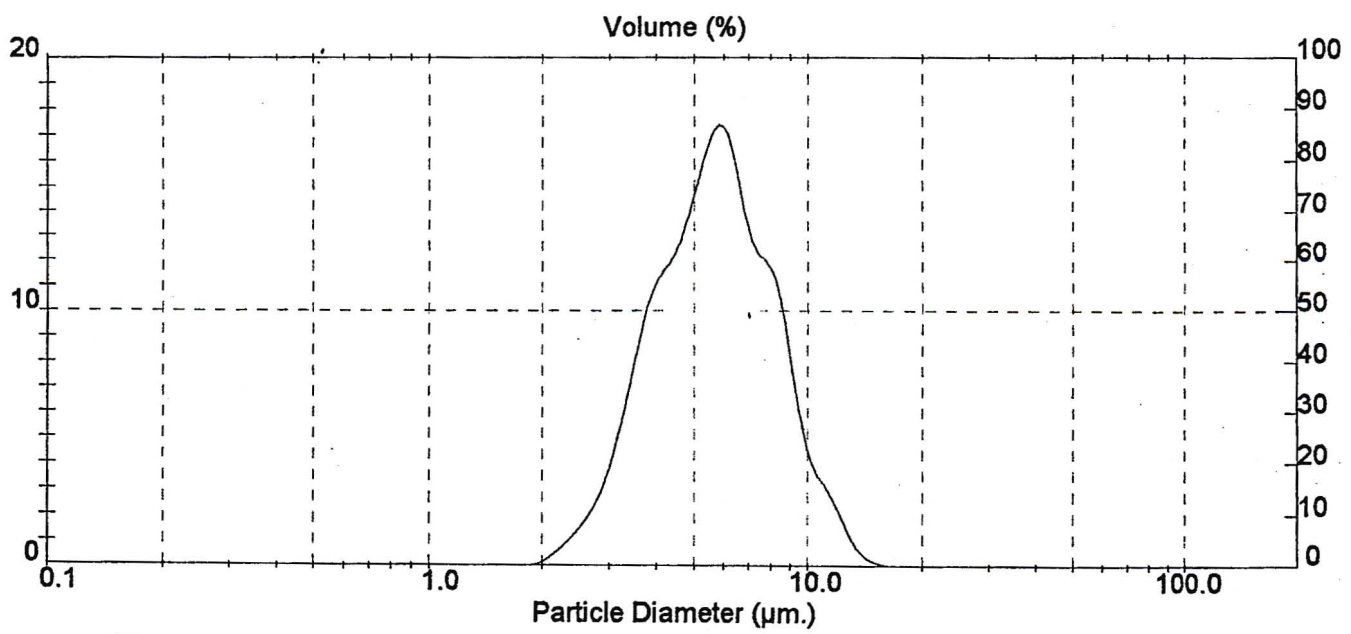

Figure C6: BASF presentation mode – 30 minutes after emulsification

Result: Analysis Report

Sample Details

Sample ID: RUN 3B - T=30
Sample File: TEST1
Sample Path: C:\SIZERMU\DATA\
Sample Notes: NEW SCALE-DOWN TANK
7500 RPM...20 MIN
7200 RPM...20 MIN
SAMPLE 4 - 40 MIN AFTER ACID ADDITION

Run Number: 4
Record Number: 1102

Measured: 10 Jan 2002 11:47
Analysed: 10 Jan 2002 11:47
Result Source: Analysed

System Details

Sampler: B
Presentation: 4OHD
Analysis Model: Polydisperse
Modifications: None

[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Measured Beam Obscuration: 20.3 %

Residual: 0.387 %

Result Statistics

Distribution Type: Volume
Mean Diameters:
D [4, 3] = 3.65 um

Concentration = 0.0069 %Vol
D (v, 0.1) = 0.54 um
D [3, 2] = 1.57 um

Density = 1.000 g / cub. cm
D (v, 0.5) = 3.82 um
Span = 1.585E+00

Specific S.A. = 3.8119 sq. m / g
D (v, 0.9) = 6.60 um
Uniformity = 4.995E-01

Size Low (um)	In %	Size High (um)	Under%	Size Low (um)	In %	Size High (um)	Under%
0.31	1.37	0.36	1.37	10.48	0.22	12.21	100.00
0.36	2.59	0.42	3.97	12.21	0.00	14.22	100.00
0.42	3.54	0.49	7.50	14.22	0.00	16.57	100.00
0.49	4.11	0.58	11.61	16.57	0.00	19.31	100.00
0.58	4.24	0.67	15.85	19.31	0.00	22.49	100.00
0.67	3.94	0.78	19.79	22.49	0.00	26.20	100.00
0.78	3.26	0.91	23.06	26.20	0.00	30.53	100.00
0.91	2.35	1.06	25.41	30.53	0.00	35.56	100.00
1.06	1.42	1.24	26.83	35.56	0.00	41.43	100.00
1.24	0.72	1.44	27.56	41.43	0.00	48.27	100.00
1.44	0.28	1.68	27.84	48.27	0.00	56.23	100.00
1.68	0.56	1.95	28.40	56.23	0.00	65.51	100.00
1.95	1.38	2.28	29.78	65.51	0.00	76.32	100.00
2.28	2.86	2.65	32.64	76.32	0.00	88.91	100.00
2.65	5.16	3.09	37.80	88.91	0.00	103.58	100.00
3.09	8.15	3.60	45.95	103.58	0.00	120.67	100.00
3.60	11.02	4.19	56.97	120.67	0.00	140.58	100.00
4.19	12.56	4.88	69.53	140.58	0.00	163.77	100.00
4.88	11.72	5.69	81.25	163.77	0.00	190.80	100.00
5.69	8.97	6.63	90.22	190.80	0.00	222.28	100.00
6.63	5.60	7.72	95.82	222.28	0.00	258.95	100.00
7.72	2.85	9.00	98.68	258.95	0.00	301.68	100.00
9.00	1.10	10.48	99.78				

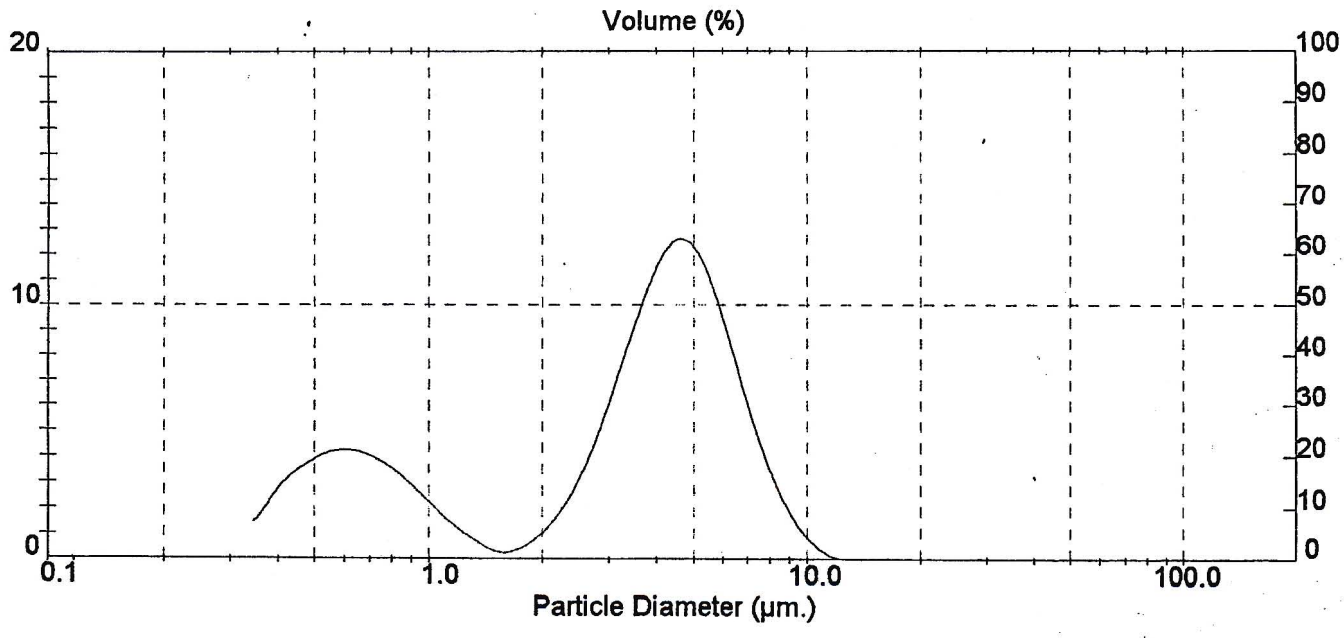

Figure C7: Mondi presentation mode – 40 minutes after emulsification

Result: Analysis Report

Sample Details

Sample ID: RUN 3B - T=30
Sample File: (Result Not Saved)
Sample Path: C:\SIZERMU\DATA\
Sample Notes: NEW SCALE-DOWN TANK
7500 RPM...20 MIN
7200 RPM...20 MIN
SAMPLE 4 - 40 MIN AFTER ACID ADDITION

Run Number: 9

Measured: 10 Jan 2002 11:47
Analysed: 10 Jan 2002 11:57
Result Source: Analysed

System Details

Sampler: B
Presentation: 4OAD
Analysis Model: Polydisperse
Modifications: None

[Particle R.I. = (1.5295, 0.0000); Dispersant R.I. = 1.3300]

Measured Beam Obscuration: 20.3 %

Residual: 0.429 %

Result Statistics

Distribution Type: Volume
Mean Diameters:
D [4, 3] = 4.54 um

Concentration = 0.0112 %Vol
D (v, 0.1) = 2.50 um
D [3, 2] = 2.88 um

Density = 1.000 g / cub. cm
D (v, 0.5) = 4.42 um
Span = 1.015E+00

Specific S.A. = 2.0842 sq. m / g
D (v, 0.9) = 6.99 um
Uniformity = 3.314E-01

Size Low (um)	In %	Size High (um)	Under%	Size Low (um)	In %	Size High (um)	Under%
0.31	0.56	0.36	0.56	10.48	0.48	12.21	99.98
0.36	1.02	0.42	1.58	12.21	0.02	14.22	100.00
0.42	1.29	0.49	2.87	14.22	0.00	16.57	100.00
0.49	1.34	0.58	4.22	16.57	0.00	19.31	100.00
0.58	1.16	0.67	5.38	19.31	0.00	22.49	100.00
0.67	0.78	0.78	6.16	22.49	0.00	26.20	100.00
0.78	0.31	0.91	6.46	26.20	0.00	30.53	100.00
0.91	0.00	1.06	6.46	30.53	0.00	35.56	100.00
1.06	0.00	1.24	6.46	35.56	0.00	41.43	100.00
1.24	0.00	1.44	6.46	41.43	0.00	48.27	100.00
1.44	0.00	1.68	6.46	48.27	0.00	56.23	100.00
1.68	0.28	1.95	6.75	56.23	0.00	65.51	100.00
1.95	1.40	2.28	8.14	65.51	0.00	76.32	100.00
2.28	3.59	2.65	11.74	76.32	0.00	88.91	100.00
2.65	7.06	3.09	18.79	88.91	0.00	103.58	100.00
3.09	11.86	3.60	30.66	103.58	0.00	120.67	100.00
3.60	13.93	4.19	44.59	120.67	0.00	140.58	100.00
4.19	15.98	4.88	60.57	140.58	0.00	163.77	100.00
4.88	16.18	5.69	76.75	163.77	0.00	190.80	100.00
5.69	10.93	6.63	87.68	190.80	0.00	222.28	100.00
6.63	5.95	7.72	93.63	222.28	0.00	258.95	100.00
7.72	4.31	9.00	97.94	258.95	0.00	301.68	100.00
9.00	1.55	10.48	99.49				

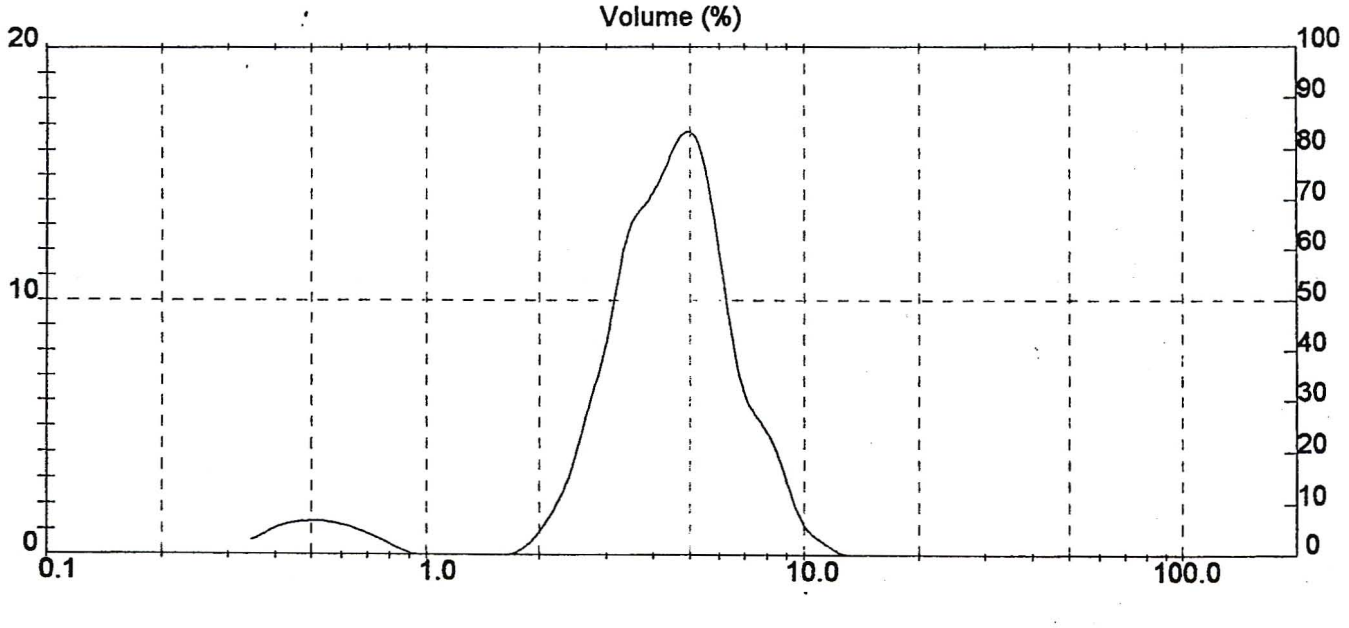

Figure C8: BASF presentation mode – 40 minutes after emulsification

APPENDIX D

The reagents used for the CB system

The chemicals discussed are specifically chosen for this process and using correct amounts of them are crucial in getting a stable emulsion. The information on the reagents was provided by Tessmer [1999] and is summarised below.

D1 Reagents for the CB system

Because carbonless copy papers are widely used in offices, it is very important that there are no side effects when handling them, e.g. sensitisation or irritation of the skin. Environmental aspects have to also be taken into account since disposal of the paper, by burning them, could lead to the chemicals unfavourably reacting with the atmosphere. For this reason chlorinated paraffin, which offers very good features for carbonless papers, was banned.

D.1.1 The colourformer solution

Materials for the colourformer solution must have special characteristics in order to produce a stable emulsion. Furthermore the chemicals used in different batches should be obtained from a constant source since their properties vary, depending on where they were obtained. This can drastically affect the properties of the microcapsules.

D.1.1.1 The dye (Pergascript)

The dye, or colourformer, which comes in powder form, should have the following properties:

- A good solubility in the solvent used.
- Low dusting.
- A minimum tendency for recrystallisation.
- A low content of insoluble parts.

The solvent, which consists of a primary solvent and a diluent, is mixed with the dye in order to form the colourformer oil. This is the ink, which is eventually encapsulated. Adding the correct amount of the dye is essential to get good image intensity. The use of too much dye can result in recrystallisation of the granules. This would then be encapsulated by the Luracoll, resulting in wastage of the chemical and a reduction in the quality of the image.

D.1.1.2 The primary solvent

A very important characteristic for the encapsulation process is that the solvent for the colourformer solution is completely insoluble in water. If the solvent is soluble in water there would not be an oil-water interface where the wall material could be deposited, i.e. there would be no encapsulation of the oil. Other features of the solvent include, a high boiling point, a low vapour pressure, little or no odour, colourless and a low viscosity. These features are consistent, with the features described in Section 2.2.4, of a good solvent.

D.1.1.3 The diluent

Due to the high price of the primary solvent, a diluent or secondary solvent is used for carbonless papers. The main features of these products are the same as that of the primary solvent, except they have little or no solubility for the dye. They also have very good solvency with the primary solvent. The main reason for its use is not only to reduce the price of the primary solvent, but also to lower the viscosity. A lower viscosity helps to transfer a larger amount of dye to the CF sheet during writing.

Mondi uses a delivered mixture as the solvent called Ruetasolv KX 8020. This is a mixture of KMC oil and kerosene type oil called Exxsol D 100, in a ratio of 80 to 20 volume per cent.

D.1.2 Emulsification chemicals

D1.2.1 Lupasol PA 140

Lupasol, which is patented by BASF in Germany, is a 20 per cent solution of a polyacrylic, sulphonic acid derivative in water. It is the substance that is partly responsible for the formation of the oil droplets in water. It stabilises the emulsion and, under sufficient agitation, gives the desired droplet size. When too little Lupasol is used low stabilisation of the emulsion can result, which in turn can result in a wider capsule size distribution. However, the use of too much Lupasol does not result in a narrower size distribution, and increases the cost of the batch. Lupasol is not a hazardous chemical. However spillage can cause the floor to be very slippery. Spillage can be washed of by using large amounts of water.

D1.2.2 Luracoll SD

Luracoll is a 70 per cent solution of methoxymethylated melamine in water. It is the wall forming material in the process and makes up 14 per cent of the capsule. An underdosage of Luracoll will weaken the capsule wall, or it may not be enough to encapsulate the entire oil droplet. This will result in free colourformer oil in the coating and very sensitive capsules. An overdosage will result in very thick and strong capsule walls. The capsules will be more difficult to break during writing and the image intensity will decrease. The overall viscosity of the batch may also be higher due to free Luracoll present in the emulsion. Luracoll contains approximately 1.5 per cent formaldehyde. The chemical itself is not hazardous, but the volatility of the formaldehyde necessitates good ventilation.

D1.2.3 Formic acid

Since a low pH is required for the formation of the capsule wall, a 10 per cent formic acid solution is used to start the polymerisation of the Luracoll around the oil droplet. It is very difficult to measure an accurate pH value in an oil / water emulsion and therefore a fixed amount and concentration of the acid is used in each batch. The pH value, in combination

with the temperature of the emulsion, has a major influence on the capsule size. A low pH results in very small capsules while a high pH causes bigger capsules, and a wider size distribution.

The addition of too much of formic acid will cause the reaction to proceed too fast, which is not favourable for a uniform capsule size distribution. The emulsification time and the agitator speed may have to be reduced to compensate for this change. The use of insufficient acid will make it difficult to initiate the polymerisation reaction since the pH will be too high. Agglomerates may form in the emulsion and a rise in the viscosity. It may also be difficult to achieve the capsules in the desired size range.

D1.3 The hardening chemicals

D.1.3.1 Ammonia and Diethanolamine (DEA)

A 25 per cent solution of ammonia is used, which increases the pH of the capsule batch during hardening. It also reacts with the free formaldehyde formed during the hardening process and reduces its amount. DEA stops the polymerisation of Luracoll, by increasing the pH of the emulsion further.

D1.3.2 Sterocoll D

This chemical is used to adjust the final viscosity of the capsule batch to between 9.3 and 9.5. It also serves as a lubricant, giving a smooth flow to the ink, whilst being coated on paper.

D.1.4 Additional materials

D.1.4.1 The buffer / spacer

During handling of the CB paper by the customer or the manufacturers, for example, rewinding, packing and transportation, the microcapsules can be easily broken resulting in smudging of the paper. Therefore a buffer, or spacer, is used in the CB formulation to protect the microcapsules from bursting before use. The resulting carbonless paper is completely insensitive during processing and handling, but gives a copy with a high image intensity. The buffer used is starch, which is spherical in shape and much larger than the microcapsules, about 20 microns in diameter. This allows for the necessary cushioning required by the capsules.

If too much of buffer is added to the CB recipe the image intensity is reduced, since there is too much protection for the capsules. On the other hand, if too little buffer is added the image intensity increases, but so does the sensitivity of the paper. Hence a correct amount of buffer has to be used, which allows optimum sensitivity of the paper. A good starch for a buffer in carbonless papers should have a narrow size distribution and should also be insoluble in water. An investigation of the effect of the starch was beyond the scope of this project.

D1.4.2 Etingal

Etingal is the final chemical added to the CB batch before it is stored. It serves as a de-foamer, removing excess foam formed during the mixing of the batch.

APPENDIX E

Example of the curves obtained for 20 different temperature experiments

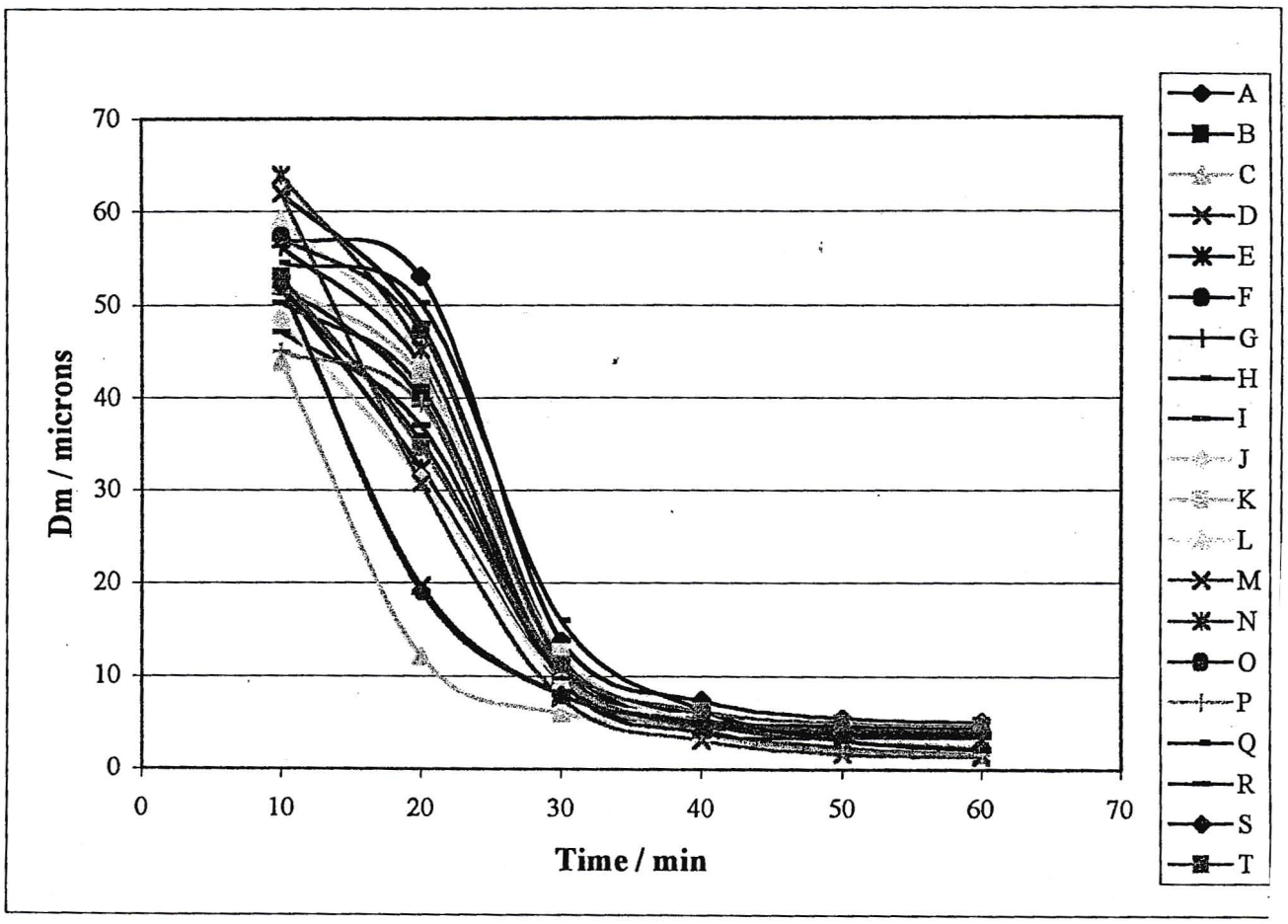

Figure E1: Reproducibility of results done at a temperature of 30 °C