



**DESIGN OF A SUNSCREEN**  
**PLANT AND THE**  
**RHEOLOGICAL STUDY OF**  
**THE EMULSION**

**SolarOz**  
Skin care

**Identification number**

112141

**Student**

Paula Corbí García

**Tutor host University**

Dr. Catherine Whitby

**Tutor home University**

Josep Chillida

11th May 2012



## ÍNDEX

1. INTRODUCTION.....	1
1.1. Abstract.....	1
1.2. Acknowledgement .....	1
1.3. Presentation.....	2
2. PRELIMINARY STAGE.....	3
2.1. Project description .....	3
2.2. Project scope .....	3
2.2.1. Final project.....	3
2.2.2. Research laboratory .....	4
2.3. Background.....	5
2.4. Initial project Planning.....	6
Gantt Chart.....	7
3. BASIS FOR DEVELOPMENT PROJECT .....	8
3.1. Database design .....	8
3.1.1. Inflow specifications.....	8
3.1.2. Capacity, operational flexibility and service on stream factor .....	8
3.1.3. Product specifications.....	9
3.1.4. Conditions of raw compounds and products in the Battery limit.....	10
3.2. Basic data for the development of engineering.....	10
3.2.1. Available utilities.....	10

3.2.2. Energy prices .....	10
3.2.3. Location of the plant.....	11
3.2.3.1. Climate, rainfall and seismic .....	12
3.2.3.2. Structure and Land Elevation .....	14
3.2.4. Design standards and codes.....	16
4. DEVELOPMENT OF BASIC ENGINEERING .....	17
4.1. Diagrams of the process.....	17
4.1.1. Conceptual design of Block Diagram.....	17
4.1.2. Simulation of the process .....	17
4.1.3. Process Flow Diagram (PFD).....	18
4.1.4. Piping and Instrumentation Diagram (P&ID) .....	18
Sheet 1: PDF .....	19
Sheet 2: P&ID T-101 .....	20
Sheet 3: P&ID T-102 .....	21
Sheet 4: P&ID T-103 .....	22
Sheet 5: P&ID AT -201 .....	23
Sheet 6:P&ID T-104.....	24
Sheet 7: P&ID Plot Plan.....	25
4.2. Basic design .....	26
4.2.1. Hydraulic design of pipes.....	26
4.2.2. Description the control strategy.....	28

4.2.2.1. De-water tank T-101 .....	29
4.2.2.2. Storage tanks for raw material T-102 and T-103 .....	29
4.2.2.3. Agitation tank AT-201 .....	31
4.2.2.4. Final product tank T-104.....	32
4.2.2.5. Relation of controllers .....	32
4.2.2.6. Relation of signals and instruments.....	34
4.2.3. Equipment design .....	34
4.2.3.1. Tanks .....	34
4.2.3.2. Agitation tank AT-201 .....	35
4.2.3.3. Pumps .....	36
4.2.3.4. Specifications Sheets.....	37
Specification Data for P101 A/B.....	38
Specification Data for P201 A/B.....	39
Specification Data for P301 A/B.....	40
Specification Data for P501 A/B.....	41
Specification Data for T-101 .....	42
Specification Data for T-102.....	43
Specification Data for T-103 .....	44
Specification Data for AT-201 .....	45
Specification Data for T-104.....	46
4.3. Process description.....	47



5.2.4.1. Viscosity test .....	62
5.2.4.2. Oscillatory .....	63
5.2.5. Results and discussion .....	64
5.2.5.1. Dispersions of laponite Rd in aqueous solution .....	64
5.2.5.2. Emulsions of bromohexadecane, aqueous NaCl and laponite RD.....	65
5.2.5.3. Microscope analysis .....	66
5.2.5.4. Rheology .....	67
5.2.5.4.1. Viscous flow .....	67
5.2.5.5. Oscillatory .....	69
5.2.5.5.1. Strain sweep test .....	69
5.2.5.5.2. Frequency sweep test.....	71
5.2.5.5.3. Dependence of laponite particle concentration .....	72
5.2.5.5.4. Dependence of storage modulus $G'$ of volume fraction.....	73
5.2.5.5.5. Breakdown test .....	73
5.2.5.5.6. Recovery test .....	74
5.3. Conclusions.....	75
6. SAFETY INSTALLATIONS.....	77
6.1. Identification hazardous zones.....	77
6.2. Protection in overpressure/vacuum equipment.....	78
6.3. Personal protection.....	78

6.4. Protections measures fire-prevention.....	89
7. ENVIRONMENT IN THE DESIGN OF THE FACILITIES.....	80
7.1. Pollutants.....	80
7.1.1. Liquid waste .....	80
7.1.2. Solid waste.....	80
7.1.3. Noise generation.....	80
7.2. Consumption of Energy and Natural Resources.....	81
8. MAINTENANCE OF THE INSTALLATION.....	82
8.1. Corrective maintenance .....	82
8.2. Preventive maintenance .....	82
8.2.1. Preventive maintenance related to time.....	82
8.2.2. Preventive maintenance related to state.....	83
8.3. Predictive maintenance .....	83
9. MANUAL OPERATIONAL .....	85
9.1. Plan production and schedule production .....	85
9.1.1. Introduction .....	85
9.1.2. Batches and Recipes .....	86
9.1.3. Routing and production monitoring .....	86
9.1.4. Production Scheduling.....	87
9.2. Start-up.....	88
9.3. Emergency shutdown.....	91

9.3.1. Failure of energy supply .....	91
9.3.2. Failure in the instrument air supply .....	91
9.3.3. Failure in cooling water supply .....	92
10. PROFITABILITY ANALYSIS .....	93
10.1. Starting data .....	93
10.2. Project implementation budget .....	93
10.2.1. Estimated cost of the equipment.....	93
10.2.2. Estimated cost of the facility .....	94
10.3. Income statement account.....	95
10.3.1. Annual income.....	95
10.3.2. Annual costs .....	96
10.4. Global investment evaluation .....	96
10.4.1. Calculation of Cash flow .....	96
10.4.2. Calculation of Net Present Value (NPV).....	97
10.4.3. Calculation of Internal Rate of Return (IRR).....	98
10.4.4. Pay Back Period (PBP) and Discounted Break-Even Period (DBEP) .....	98
10.5. Conclusions of profitability analysis .....	99
11. REFERENCES.....	100
<b>APPENDIX</b>	
A1.PIPING DESIGN.....	103
A1.1. Basic design.....	103

A2. DESIGN OF THE PUMPS.....	104
A2.1. Mechanical energy balance.....	104
A2.2. Calculation of NPSH available.....	105
A3. EQUIPMENT DESIGN.....	106
A3.1. Basis for designing the tanks .....	106
A3.2. Calculation of the Thickness .....	106
A3.2.1 Lids .....	107
A3.2.2 Walls of the tanks .....	107
A3.2.3 Weigh of the tanks .....	108
A3.3. Design of jacket of agitation AT-201 .....	108
A4. ARTICLE .....	112
A5. PROFITABILITY ANALYSIS.....	120
A5.1. Protect implementation budget.....	120
A5.2. Income and costs .....	121
A5.3. Global investment evaluation .....	123
A6. THE SUNSCREEN INDUSTRY IN AUSTRALIA: PAST, PRESENT, AND FUTURE.....	124
A6.1. Introduction .....	124
A6.2. Standards Australia and sunscreens.....	124
A6.3. Sunscreen products: evaluation and classification .....	126
A6.4. Classification of sunscreens.....	126
A6.5. Sunscreen Categories.....	126

A6.6. Broad-spectrum sunscreens .....	127
A6.7. Water-Resistant Sunscreens.....	128
A6.8. Government regulations.....	128
A6.9. Anticancer councils and sunscreens .....	129
A6.10. Sunscreens in the future.....	129
A7. MATERIAL SAFETY DATA SHEET .....	130
A7.1. Laponite XGL.....	130
A7.2. Dow Corning .....	135
A7.3. Pure Thix HH.....	141

## **1. INTRODUCTION**

---

<b>Title of the project</b>	Design of a sunscreen plant and the rheological study of the emulsion
<b>Number</b>	112141
<b>Date</b>	11 <sup>th</sup> of May 2012
<b>Location</b>	Adelaide, Australia
<b>Author</b>	Paula Corbí García

---

### **1.1. Abstract**

SolarOz has designed a sunscreen production plant with a production of 500 tones/year, located at the outskirts of Adelaide, Australia. This plant produces three different products employing the batch system, in order to make the project financially feasible.

The sunscreen elaboration process follows a receipt divided in 4 phases. The process involves an agitation tank working at different temperatures, 17 °C and 60 °C, according to the recipe specifications. Following the receipt, the components are being added and mixed during a concrete period of time, depending on the phase, until reaching homogeneity. This process takes 5.34 hours between loading, mixing and unloading.

When the sunscreen is ready, it is sent to the bottling plant or the storage tank, which depends on the market demand.

For the design of all the equipment involved in the process, the normative and codes under the Australian legislation are used.

The total plant investment rises up to 1.4 M AUD\$, with an opportunity cost of 8%. The amortization period has been fixed in 10 years. As reported by the results of the profitability analysis, the invested capital will be recovered in 5 years.

### **1.2. Acknowledgement**

I would like to thank my friends and my family for their support and contribution to myself and my project. I would also like to say a special thank you to my supervisors Dr. Catherine Whitby at Ian Walk, University of South Australia, and Josep Maria Chillida for their guidance throughout the practical work of this project without whom would not have

been possible. Finally, I would like to thank Paul Ruschitzka, Francesc Queralt and Tom Allison for their help in the write-up of this project and Sergio Gutierrez in printing.

### **1.3. Presentation**

I coursed an internship at the Ian Wark Research Institute, at the University of South of Australia, in Adelaide; where I worked on the stability and flow behaviour of emulsions using laponite as an emulsifier under the supervision of Dr. Catherine Whitby.

My aim is to do an integrated external project; therefore I will develop an external Final Project and an external Research Laboratory. Rationale for choosing this project was to ensure the maintenance of a relationship between work experience (Research Laboratory) and project aims (Final project).

In the Research Laboratory we investigated the thixotropic behaviour of laponite dispersions and emulsions stabilized by laponite particles.

Thixotropy can be defined as the tendency of matter to exhibit a time-dependent change in its reference properties (viscosity, yield value, time scale, elasticity modulus, loss modulus). A thixotropic fluid is a fluid which takes a finite time to attain equilibrium viscosity when introduced to a step change in shear rate. Thixotropic behaviour is commonly encountered in emulsions used in creams, sauces, inks and drilling muds. Understanding the mechanisms that cause this complex rheological behaviour is of vital importance when using materials and in controlling the industrial processes in which they are involved (ref. 1). Therefore, for the final project we will focus on sunscreen emulsion. We chose to design a sunscreen plant, which focus within our research area, where laponite is used as an emulsifier in the manufacturing of sunscreen.

## **2. PRELIMINARY STAGE**

### **2.1. Project description**

The project is based on the design of a sunscreen plant and the rheological study of one of the emulsifier of the emulsion. The production plant produces 500 tons per annum (ref. 2) of sunscreen. This plant works in batch campaigns which lengths depends on the market demand. The rest of the time the plant procedures are considered outside of the scope of this project.

The reason for developing this project is to apply the knowledge achieved from experiments, working with laponite to understand the properties of the sunscreen and how it is made, also to determine the best process conditions to allow more control over the properties of sunscreen (ex. texture).

### **2.2. Project scope**

#### **2.2.1. Final project**

As already mentioned, the project will focus on the study and design of a sunscreen plant and the design of the agitation tank where emulsion takes place.

The battery limits involves, the agitation tank, the storage tanks of the raw materials and final product of the sunscreen.

The main objectives are:

- Design of the agitation tank (size, material, tank specifications...).
- Study of the emulsion processes.

A comprehensive study will be conducted on this unit including:

- Basic equipments design (storage tanks, pumps and piping).
- Operating parameters (densities, viscosities, flows, etc).

- Maintenance and scheduling of the production.
- Control strategy of the main equipment (storage tanks and agitation tank).

Moreover, the project will also include the study and overview of the whole plant. This includes environmental, economic and safety study, overview description for other process units involved and the real planning related to project development.

In addition, a Block Diagram, Process Flow Diagram (PFD), Piping and Instrumentation Diagram (P&ID) and a simulation using SuperPro software are included.

The parts not considered in this project are:

- Logistics (loading, unloading, etc).
- Process specification of the others products (A and B).
- Park of tanks.
- Sizing of valves.

### **2.2.2. Research laboratory**

As, already mentioned, the aim of the research laboratory is to study the stability and flow behaviour of emulsions using laponite. An emulsion is stabilized by solid particles (in that case laponite) which adsorb onto the interface between two phases. In dispersion small droplets of oil phase are formed and dispersed throughout the water. However, if solid particles are added to the mixture, they will bind to the surface of interface and prevent droplets from coalescing, thus causing the emulsion to be more stable (ref. 3).

The specific objectives related to the Research Laboratory are:

- To study the use of particle dispersions (laponite) to stabilise emulsions and study its flow behaviour.

Below, you can see the procedure that we will follow:

1. Establish if laponite dispersions can be used to stabilise emulsions.
2. Reproducibly measure the rheological properties (viscous flow, oscillatory) of dispersions.

3. Quantify the thixotropic behaviour of dispersions.
4. Reproducibly measure the rheological properties of the emulsions.
5. Compare thixotropic behaviour of particle-stabilised emulsions to that of dispersions.
6. Prepare report on results.

### **2.3. Background (ref.4-5)**

Sunscreen has been around longer than most of us realise. The first reported use of sunscreen was in the United States in 1928, with the commercial introduction of an emulsion containing, benzyl cinnamate and benzyl salicylate, two sun screening chemicals. At the beginning of the 1930s, a new product appeared on the Australian market containing 10% Salol (phenyl salicylate). In 1936, in France, a chemist called Eugene Schueller introduced the first commercial suncreening product; he was the founder of L'Oreal cosmetic company.

The first sunscreen patent was in 1943, leading the way for the incorporation of p-aminobenzoate derivatives in sunscreen formulations. Austrian scientist Franz Greiter is additionally named as an inventor of sunscreen, a product named Glacier Cream. Greiter was inspired to create a product in 1946 to protect the skin from sunburn due to a burn he received while mountain climbing at Piz Buin, on the Swiss-Austrian border, eight years prior. Others even attribute the invention of sunscreen to Benjamin Green. In the 1940s, Green, a Miami, physician, prepared a red jellylike substance in his own kitchen and then tried its effectiveness on his own bald head. Green was interested in protecting WWII soldiers stationed in the South Pacific. In the history of sunscreen, another important date was the invention of zinc cream in 1940.

During World War II red petrolatum was used by the U.S. military, which led to the extensive use of both physical and chemical ultraviolet filters after the war. Another sunscreen appeared on the market in the 1960s. Its purpose was to attempt to minimize the effects of ultraviolet light from the sun. However, it wasn't until around 1972, that this sunscreen was introduced in the U.S, which leads to the labeling of the sun protection factor.

(SPF). These sunscreens, which were improved and modified over time, were designed to block ultraviolet-B radiation.

After the war, Green continued to experiment with his sunscreen formula until he created what became known as Coppertone suntan cream in 1944. Coppertone suntan cream, scented with jasmine, was the first consumer mass-produced sunscreen product.

Then it wasn't until the late 1980s that researchers determined that although ultraviolet-B light initiates most skin cancers, ultraviolet-A rays also play a role in promoting skin cancer. So, in the early 1990s, sunscreens were improved to contain ultraviolet-A blockers via an ingredient called Parsol 1789. In the mid 1990s, ultramicronized zinc and titanium oxide were added to many sunscreens.

Over the years, many sunscreen variations have been developed: waterproof, spray-on, disappearing coloured sunblock for kids, and day-long protection. The requirements for sunscreens vary by country. The standards for U.S. sunscreens are lax compared to those required by Australia. Sunscreens in Australia must withstand two hours of rapidly moving water, which prevents wash off or sweat off. U.S. standards require effectiveness only for 30 minutes of standing water.

#### **2.4. Initial project Planning**

The project planning has been done by the use of a Gantt chart. Gantt Chart displays the duration of each task, the starting dates and deadlines, as well as the total time required for the implementation of the project.



### **3. BASIS FOR DEVELOPMENT PROJECT**

#### **3.1. Database design**

The following chapters provide all necessary information for the proper development of this project.

##### **3.1.1. Inflow Specifications**

The De-Water (deionised water) inflow to the sunscreen plant is 608 kg per batch. The water is supplied by another company close to this plant. The De-Water is warmed in T-101 and flows to the agitation tank AT-201, where the other ingredients are added accordingly to table 3.1.

Table 3.1. Raw materials of sunscreen.

<b>Phase</b>	<b>Raw Material/ INCI</b>	<b>% Weight</b>	<b>Trade Name</b>
<b>A</b>	Water	60.8	Deionised water
	Sodium Magnesium Silicate	0.8	Laponite XLG
	Bentonite	2	Gelwhite L
	Bentonite and Xanthan Gum	0.2	Optigel WX
<b>B</b>	Citric Acid	0.2	Citric Acid
<b>C</b>	Dow Corning 200 350 cst	20	Dow Corning
	GranLux TEMS 45T	10	Titanium dioxide
	Glycerine	0.5	Glycerine
<b>D</b>	Preservative	0.5	Dowicil 200
	1,3 Butylene Glycol, water, Polyether-1	5	Pure Thix HH

##### **3.1.2. Capacity, operational flexibility and service on stream factor**

As already stated, the project consists of the design of a multiproduct batch plant, where besides the sunscreen other products are manufactured. The table 3.2 shows the complete product palette. The production capacity is the same for all the products, being the manufacturing process very similar in all cases.

Table 3.2. Other products produced by the company.

Product	Production (Tm/year)
Sunscreen	500
B	500
C	500

The database designs for this plant consider those only for the production of sunscreen and not the other products mentioned. Data designs of the plant are as follows:

- Capacity shear dedicated to sunscreen: 500 t/year.
- Nameplate capacity: 1,500 t/year.
- On stream factor of sunscreen product: 2,667 h/year.
- On stream factor of A: 2,667 h/year.
- On stream factor of B: 2,667 h/year.
- Total on stream factor: 8,000 h/year.

### 3.1.3. Product specifications

In this process the product specifications are given for quality control, quantities and the properties that the sunscreen should have.

The sunscreen industry is extremely well regulated. Both self-regulation and thorough monitoring by the Food and Drug Administration (FDA) in the United States and The Cosmetic Europe – The personal Care Association previously called COLIPA in European Union (EU). In the case of non-EU countries, Japan, Asia, Canada and Australia, this is controlled, by governmental agencies. In Australia this is known as the Therapeutic Goods Administration. For more details see appendix 6.

The properties, as viscosity, density, colour, etc., have been monitored, but a determinate value has not been established. As follows, table 3.3 shows the properties that in this case have been accomplished.

Table 3.3. Quantitative properties of sunscreen.

Parameters	Approved valour
Titanium dioxide	2-25* %
Ph	6-7,5

\*Titanium Dioxide at this concentration causes unacceptable skin whitening.

### **3.1.4. Conditions of raw compounds and products in the Battery limit**

The raw materials and final product conditions in the battery limit are: room temperature (17 °C) and atmospheric pressure.

## **3.2. Basic data for the development of engineering**

This chapter presents all data necessary for project development. It shows the available location of the sunscreen plant.

### **3.2.1. Available utilities**

As follows, it is explained the utilities that the plant has. It is important to remark that this plant does work with steam neither fuels.

- Power supply: three-phase electric current at 50 Hz and 380 V.
- The cooling water is supplied by another company at 3.5 kg/cm<sup>2</sup> and 20 °C temperatures and it is returned at 45 °C.
- Instrumentation air is atmospheric air and is supplied at room temperature. The dew point is -20 °C, to avoid condensation and 5 atmospheres.
- Dry nitrogen is supplied at room temperature and 7 kg/cm<sup>2</sup>. The dew temperature is -20 °C.

### **3.2.2. Energy prices**

The prices for the energies are in table 3.4. These prices are obtained from the Government of South Australia's website. (ref. 6).

Table 3.4. Utilities Prices.

<b>Utility</b>	<b>Price (AUD\$)</b>
Cooling water (m <sup>3</sup> )	0.17
Power (kWh)	0.123
Air instrumentation (m <sup>3</sup> N)	0.007
Nitrogen (m <sup>3</sup> N)	0.05

**3.2.3. Location of the plant**

After a study evaluating the different alternatives, it was decided to locate the production plant in a small chemical complex dedicated to small industrial, analytical, cosmetic, food and beverage and laboratory reagent chemicals, in Camden Park next to the city of Adelaide.



Figure 3.1. Map of Australia.

Adelaide has an area of 1,826.9 km<sup>2</sup> and a population of 1,203,873 inhabitants (2010). The following table 3.5 shows the technical details of the location.

Table 3.5. Technical data of Adelaide.

Characteristic	Value	Characteristic	Value
Longitude	138°36'3.6" E	Country	Australia
Latitude	55 44.4" S	State	South Australia
Perimeter	1.13 km	Capital of state	Adelaide
Area	0.0735 km <sup>2</sup> (0.362 km x 0.203 km)	Postal Code	SA 5038

The following picture shows the location of the plant with an orange cross, inside de suburbs of Adelaide city.



Figure 3.2. Map of plant location.

### **3.2.3.1. Climate, rainfall and seismic**

Adelaide has a hot-summer, where most of the rain falls in the winter months. Of the Australian capital cities, Adelaide is the driest, and it has a semi-arid climate influence because of its dryness. Rainfall is unreliable, light and infrequent throughout summer. In contrast, the winter has fairly reliable rainfall with June being the wettest month of the year; averaging around 80 mm. Frosts are occasional, with the most notable occurrences having occurred in July 1908 and July 1982. Hail is also common in winter. There is usually no appreciable snowfall, except for very light falls at Mount Lofty and some places in the Adelaide Hills.

Figure 3.3 shows temperature, rainfall, wind speed and the relative humidity average values during 2007.

The important data relating to the climate in Adelaide (ref. 7) is shown figure 3.2 and is explained as follows:

- The average temperature in Adelaide, Australia, is 17.0 °C.
- The highest monthly average high temperature is 29 °C in January and the lowest monthly low temperature is 7 °C in July.

- Adelaide's climate receives an average of 523 mm of rainfall per year, or 44 mm (1.7 in) per month. On average there are 121 days per year with more than 0.1 mm (0.004 in) of rainfall (precipitation) or 10 days with a quantity of rain, sleet, snow etc. per month.
- The driest weather is in March when an average of 21 mm (0,8 in) of rainfall (precipitation) occurs across 5 days. The wettest weather is in May when an average of 66 mm (2.6 in) of rainfall (precipitation) occurs across 13 days.
- The average annual relative humidity is 45.8% and average monthly relative humidity ranges from 31% in January to 64% in June.
- Average sunlight hours in Adelaide range between 4.1 hours per day in June and 10.0 hours per day in January.

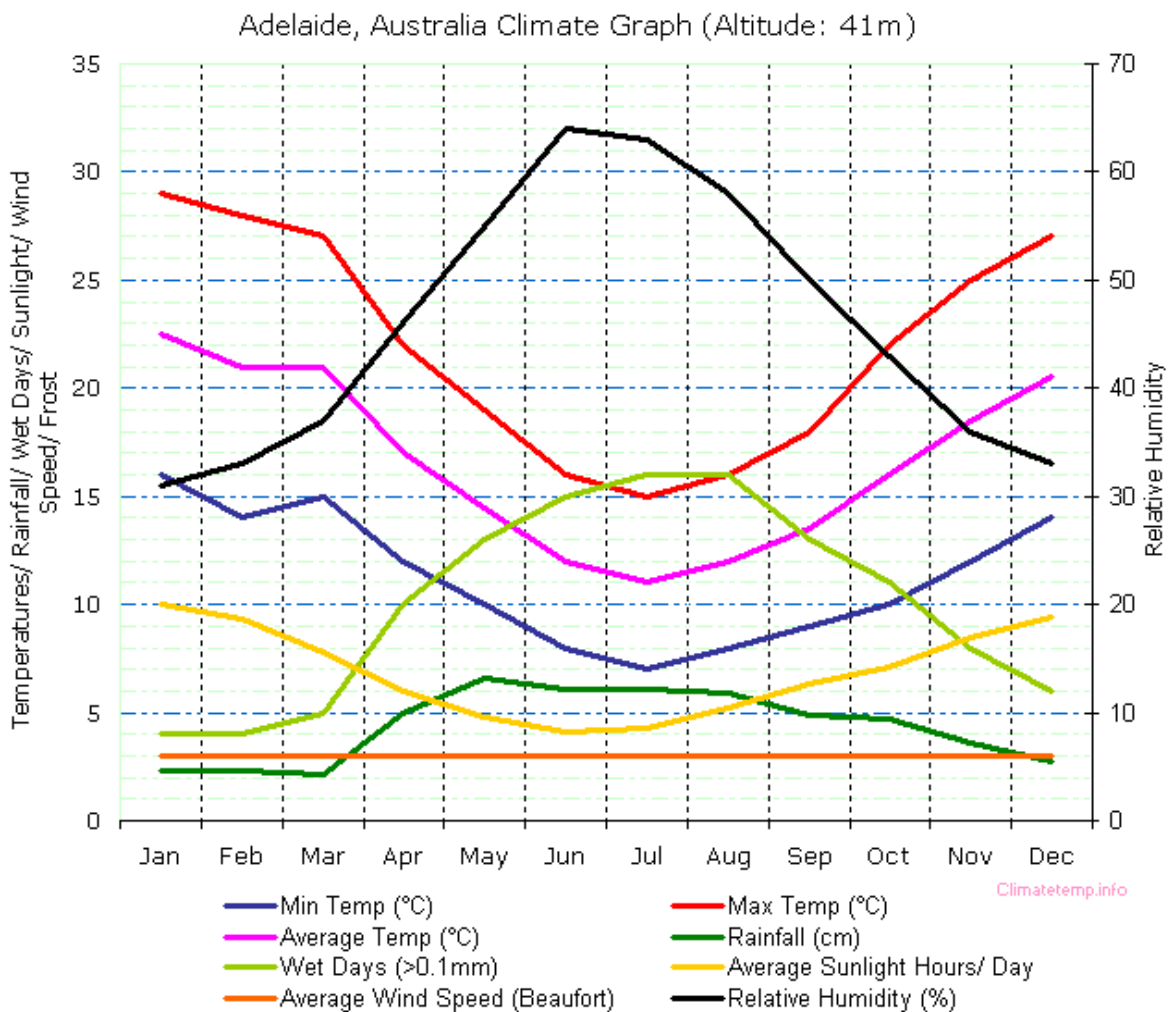


Figure 3.3. Data average of temperature, rainfall and relative humidity.

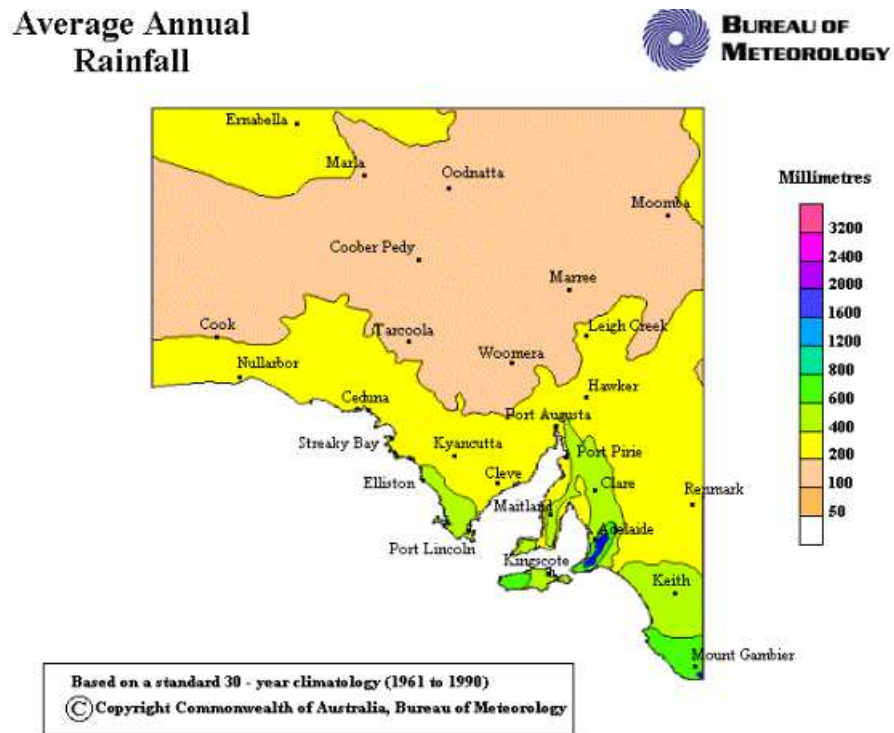


Figure 3.4. Average annual rainfall in South Australia.

The location of the plant has shown to not be vulnerable to serious seismic problems. There have been very few earthquakes occurring near Adelaide over the last decade; only about 1 per year within 30 km of the city. The low accuracy with which the epicentres can be calculated makes it difficult to tell if the events that have occurred are on the major fault lines near Adelaide.

Soft, deep sediments amplify earthquake vibrations. Fortunately most of the Adelaide metropolitan area is underlain by fairly stiff sediments; however some amplification will still occur. Deep sediments under the city will also cause some amplification for tall buildings. The intensity map of the 1954 earthquake did not however show any areas of very strong amplification. There was some damage from the 1954 event to buildings on soils in steeply sloping area (ref. 8).

### **3.2.3.2. Structure and Land Elevation**

The terrain is mostly low plateau with deserts while the fertile plain is in southeast. This map of Australia shows the geographical landscape of the country as well as the distribution of cities.

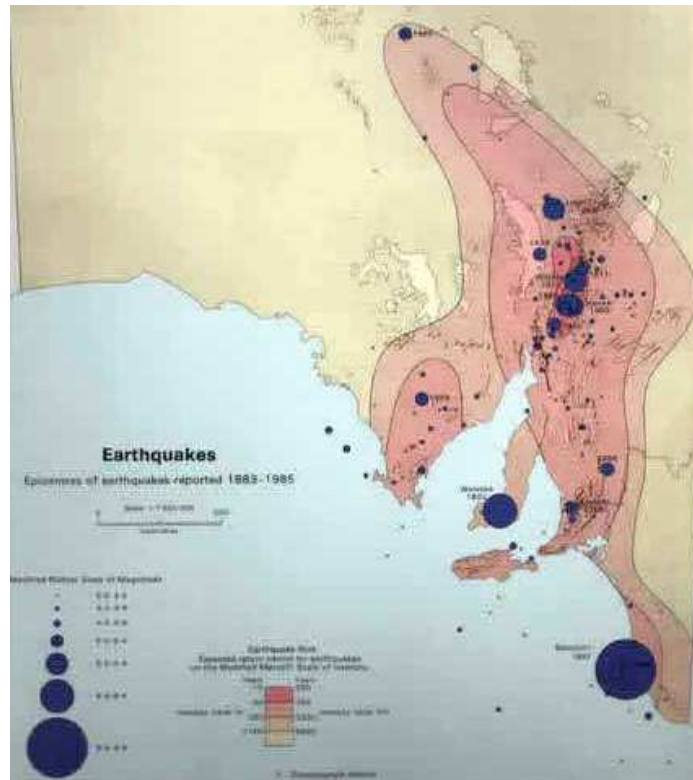


Figure 3.5. Map of seismic zones of South Australia.



Figure 3.6. Geographical landscape map of Australia.

One can see in figure 3.6, that Adelaide is surrounded by a plateau. Adelaide is placed 50 m above sea level.

### **3.2.4. Design standards and codes**

For sizing equipment, containers, pipes and their subsequent implementation and electricity consumption, the following standards and codes have been used:

- Equipment and pressure vessels: ASME Code Section VIII, Division I.
- For the determination of the distances between the equipments have used the ITC-MIE APQ-001APQ and Guidelines in Australia.
- Pumps are designed in relation to API 610.
- The piping systems are designed according to ASME B31.1 “Power design” and also ASME B31.3 “Process design” codes.

## **4. DEVELOPMENT OF BASIC ENGINEERING**

### **4.1. Diagrams of the process**

#### **4.1.1. Conceptual design of Block Diagram**

Basically, the sunscreen process is divided into 3 units: one unit involves raw material storage. This unit can be further divided into raw materials, which are kept in tanks, and others including liquids or powders. The second unit involves mixing, which works at different temperatures and the third unit is product storage. Deionised water moves into the agitation tank, where phase A is added and mixed until uniform. Then, phase B is added homogenized and the cooling process starts. In the same vessel phase C and finally phase D are added. Once the sunscreen is thoroughly mixed, the mixture is sent to a storage tank and then, sent to be bottled. After passing the quality control the product is ready for sale.

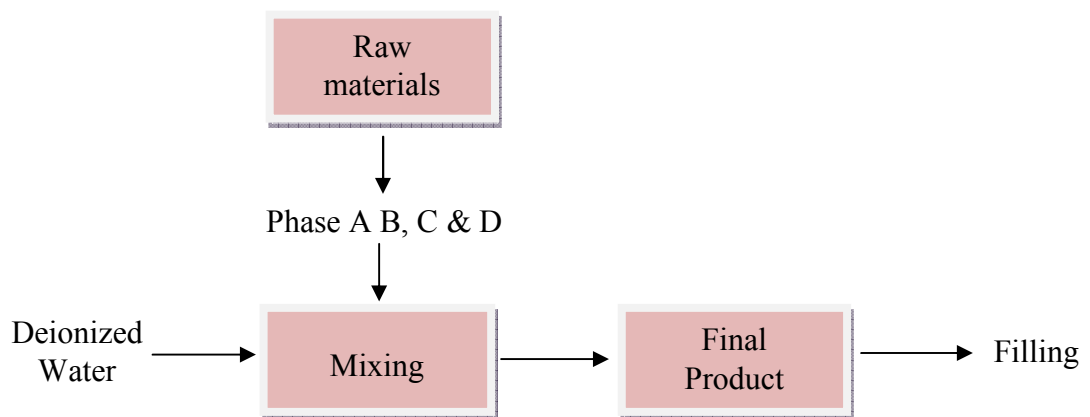


Figure 4.1. Block diagram of sunscreen process.

#### **4.1.2. Simulation of the process**

According to the Guidance and the compulsory requirements of the final project, a simulation of the process has been conducted, using the SuperPro software (only software available for batch process). However, due to the type of process, it was not possible to carry out a proper simulation. Since SuperPro does not have a data base of solid compounds,

neither the capacity to work with simultaneous processes, like the cooling process and mixing process at the same time, etc. For this reason, the simulation could have not been performed.

#### **4.1.3. Process Flow Diagram (PFD)**

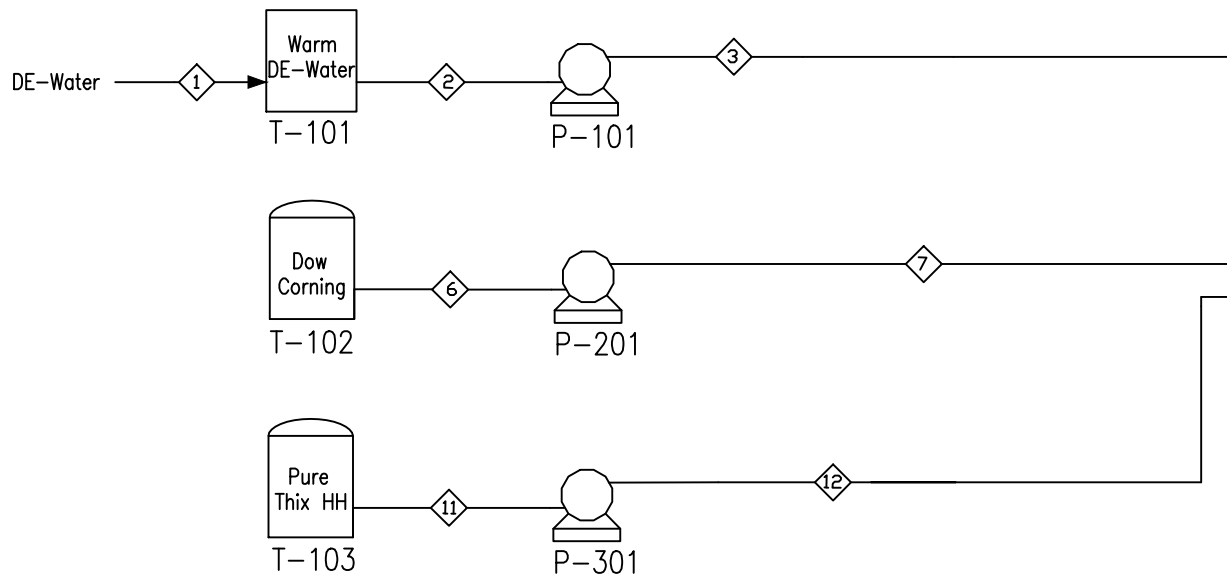
Process Flow Diagram (PFD) shows the main equipments involved in the production process of sunscreen. It outlines briefly the different zones of the plant, such as the storage of the raw materials, the agitation tank and finally, the final product tank. The materials not stored in tanks are added by feed hopper at the top of the agitation tank.

The Process Flow Diagram shows the streams numbered, balance flow in kilograms per batch of each material, conditions of the process (pressure and temperature) and state of all components (liquid or solid). This is corresponded in sheet 1.

#### **4.1.4. Piping and Instrumentation Diagram (P&ID)**

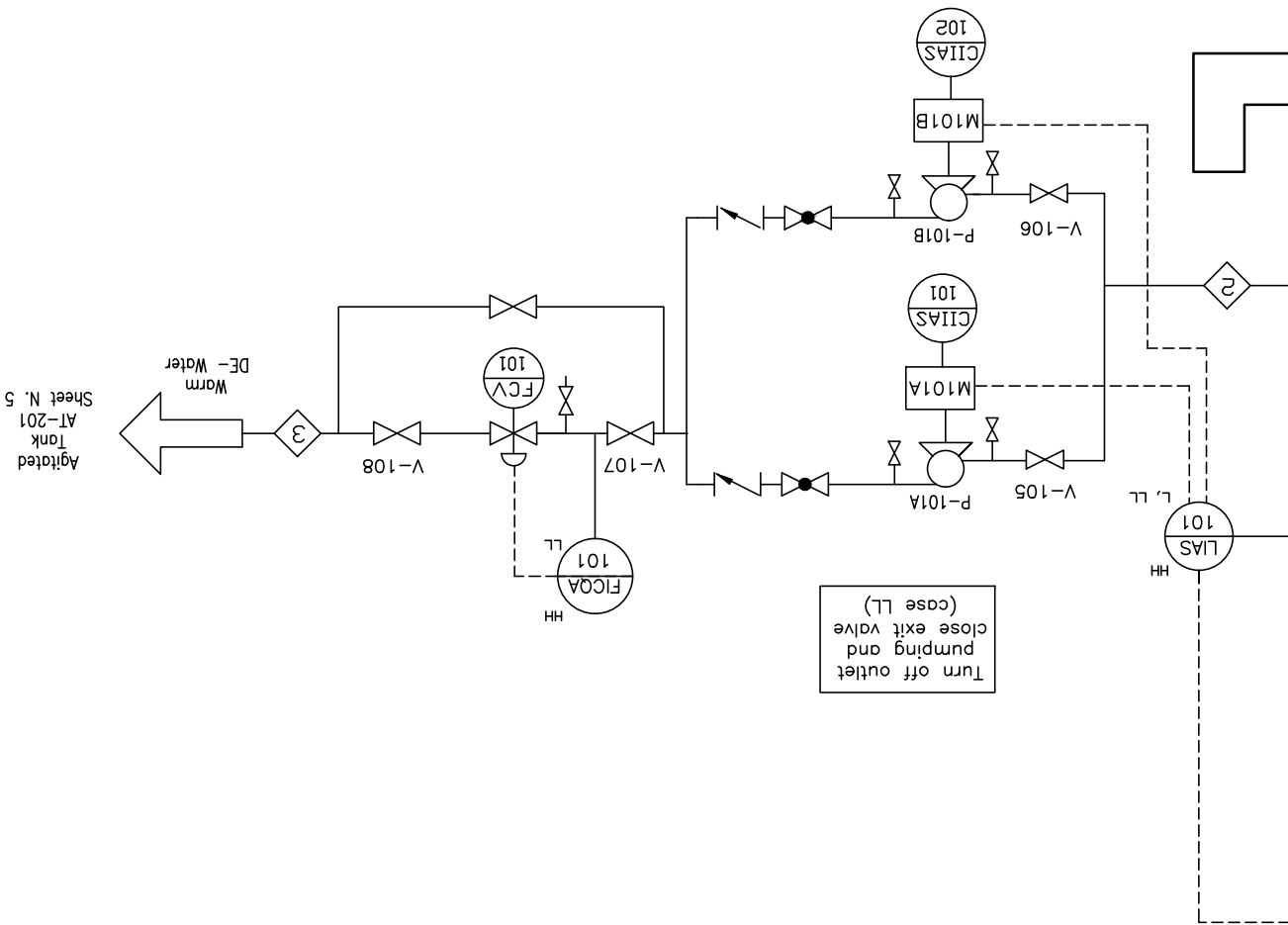
The P&ID shows all equipments that the plant uses, each process line, instrumentation, safety valves, control valves, and all the additional valves installed in the plant. Each equipment has its own P&ID, known as, T-101, T-102, T-103, AT-201 and T-104 are shown by sheets 2, 3, 4, 5 and 6, respectively.

Phase	Stream					1	2	3	4	5
	Compound (kg/batch)									
A	Deionized water					608	608	608	0	0
	Laponite XLG					0	0	0	8	0
	Gel white L					0	0	0	20	0
	Opigel WX					0	0	0	2	0
B	Citric Acid					0	0	0	0	2
C	Dow Corning					0	0	0	0	0
	Titanium Dioxide					0	0	0	0	0
	Glycerin					0	0	0	0	0
D	Dowicil 200					0	0	0	0	0
	Pure Thix HH					0	0	0	0	0
Conditions	Total					608	608	608	30	2
	Temperature (°c)					25	60	60	25	25
	Pressure (atm)					1	1	1	1	1
	State					Liquid	Liquid	Liquid	Powder	Liquid



T-101	Warm DE-Water Tank	H-201	Feed Hopper
T-102	Dow Corning Tank	P-101	Pump for warm DE-Water
T-103	Pure Thix HH Tank	P-201	Pump for Dow Corning
T-104	Final product Tank	P-301	Pump for Pure Thix HH
AT-201	Agitated Tank	P-501	Pump for Final Product

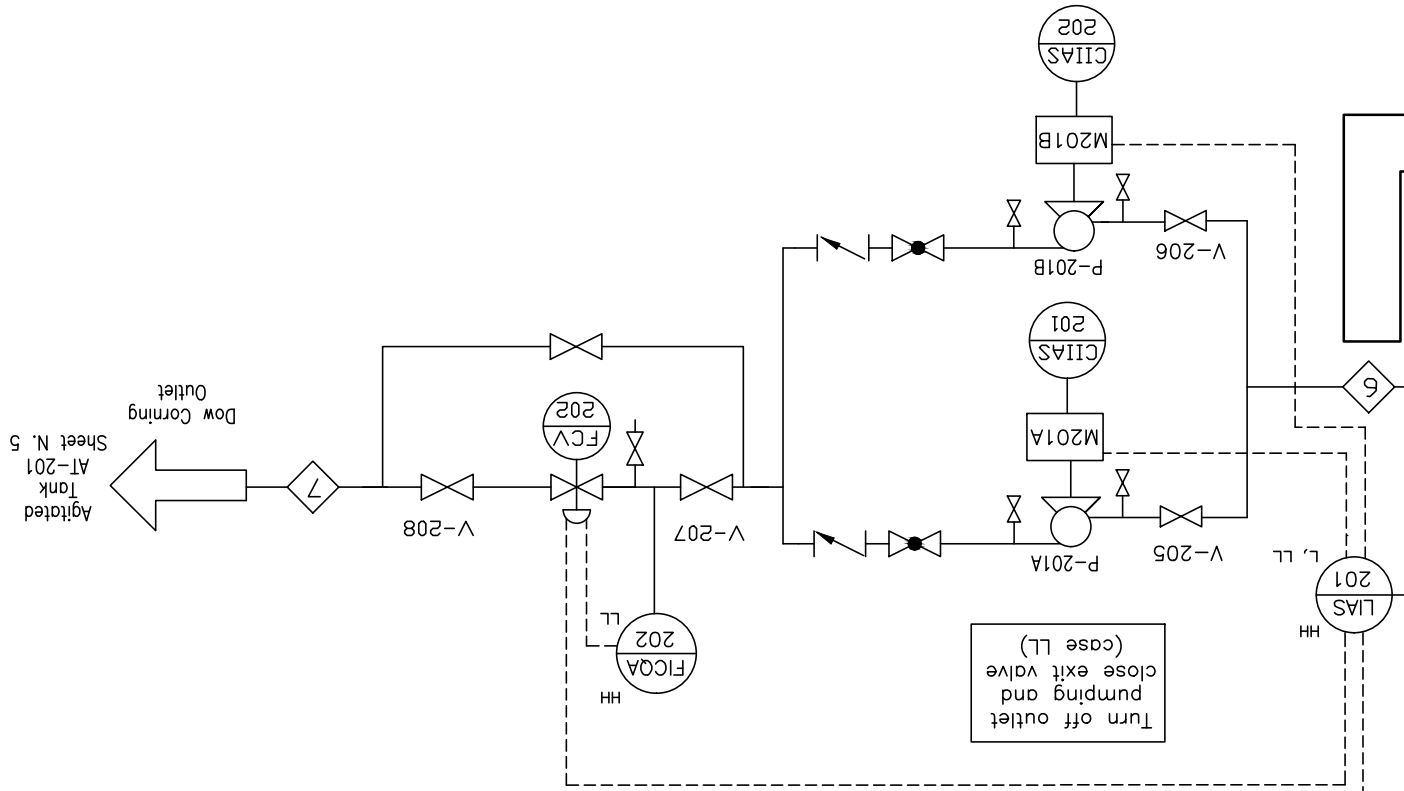
Substituted by	Substituted from	Nº 2	P&ID T-101		Scale			
						Drawn	11/05/12	Solaroz
						Checked		
UNIVERSITAT ROVIRA I VIRGILI			Pag. 20	Data	Norm			



Agitated Tank AT-201 Sheet N. 5

Turn off outlet pumping and close exit valve (case LL)

Scale	P&ID T-102		S. Codes	
	Substituted from			Checked
	Nº 3			
Drawn	11/05/12	Pag. 21	UNIVERSITAT ROVIRA I VIRGILI	
Data	Norm			

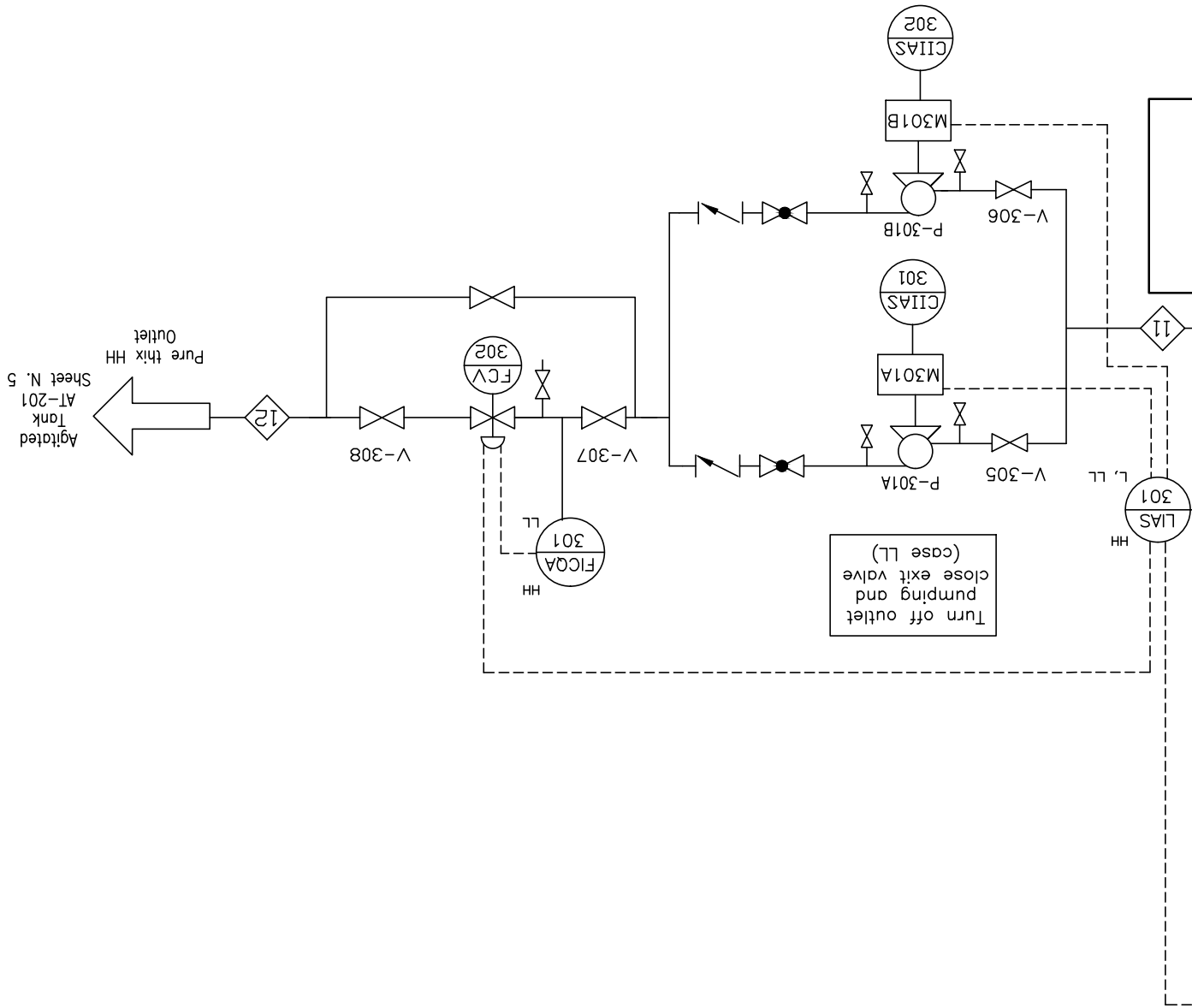


Agitated Tank AT-201  
Sheet N. 5

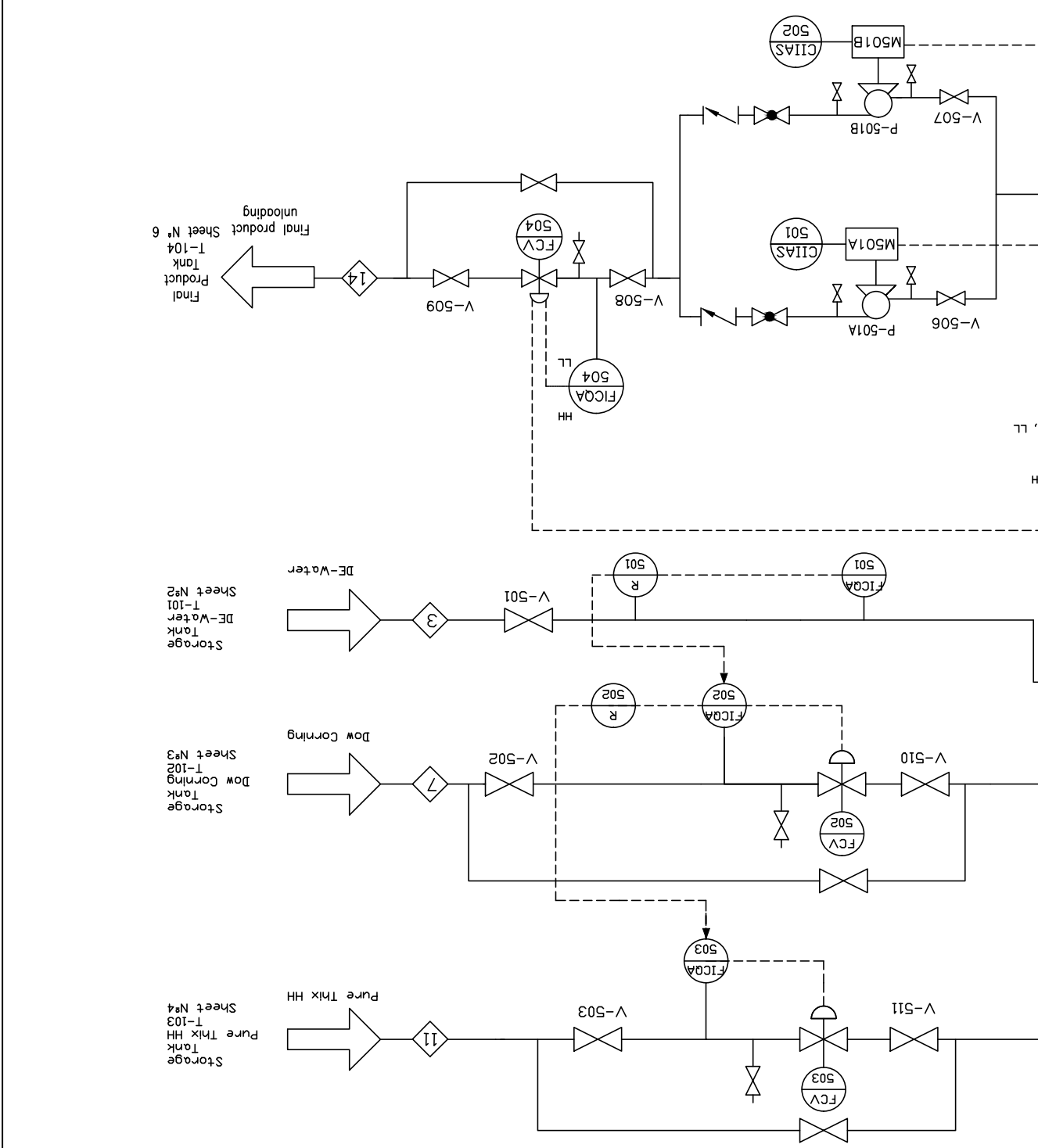
Dow Corning Outlet

Turn off outlet pumping and close exit valve (case LL)

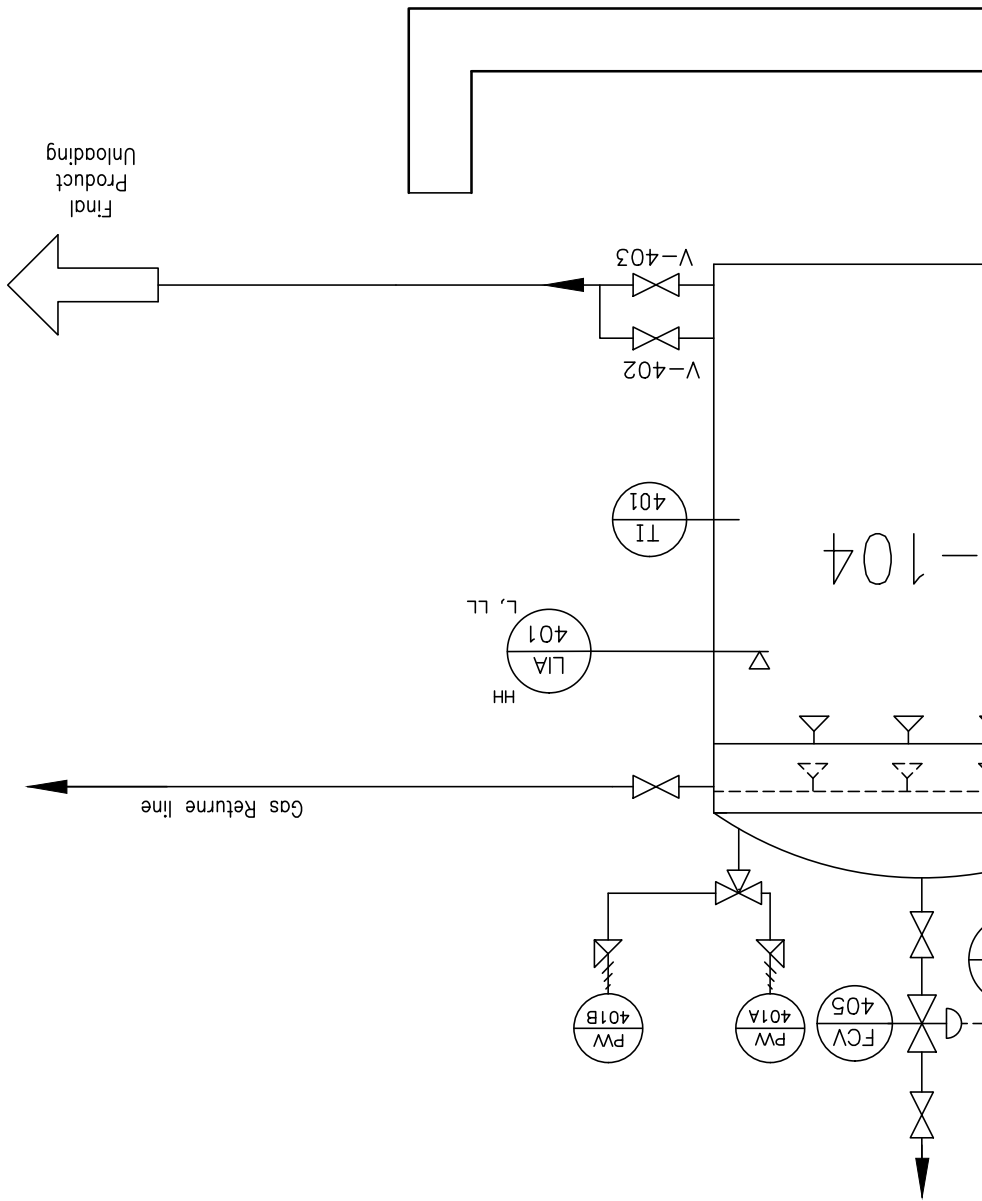
Substituted by	Substituted from	N° 4	P&ID T-103		Scale			
						Drawn	11/05/12	Solaroz
						Checked		
UNIVERSITAT ROVIRA I VIRGILI			Pag. 22	Data	Norm			

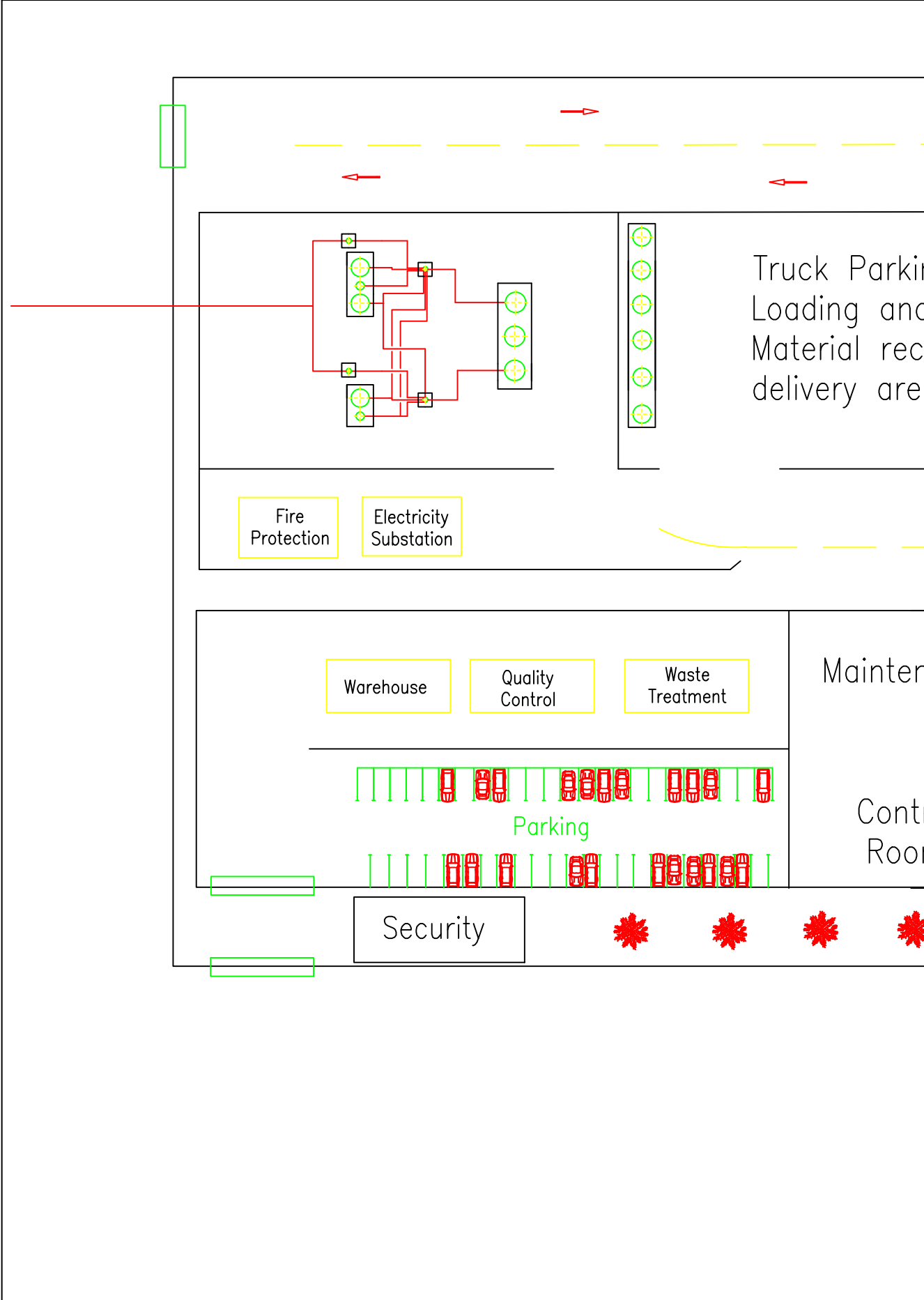


Scale	P&ID AT-201		S. Codes	
	Substituted from			Checked
	Substituted by			
Drawn	11/05/12	Pag. 23	Data	
	Solaroz			Norm
UNIVERSITAT ROVIRA I VIRGILI				



Substituted by	Substituted from	N° 6	P&ID T-104				Scale				
								Drawn	11/05/12	Solaroz	
								Checked			
UNIVERSITAT ROVIRA I VIRGILI			Pag. 24	Data	Norm	S. Codes					





## 4.2. Basic design

### 4.2.1. Hydraulic design of pipes

The piping systems are designed according to ASME B31.1 “Power design” and also ASME B31.3 “Process design” codes.

As already mentioned, there are raw materials in powder form. These materials are considered soluble in water, except for Titanium Dioxide that is partially soluble under the working conditions. In addition, the weight percentages are less relevant as can be seen in table 4.1, therefore it is considered that they do not affect considerably the viscosity and density, instead they are considered to have the same properties as water. All pipes that are inside the battery limit have 90° elbows.

Table 4.1. Powder compounds for sunscreen.

<b>Materials/INCI Name</b>	<b>Trade Name</b>	<b>% Weight</b>
Sodium Magnesium Silicate	Laponite XLG	0.8
Bentonite	Gelwhite L	2.0
Bentonite and Xanthan Gum	Optigel WX	0.2
GranLux TEMS 45T	Titanium dioxide	10.0
Preservative	Dowicil 200	0.5

Table 4.2 shows the name of all the pipes and all characteristics parameters which are in the battery limits.

In Appendix 1, there is the method used to calculate the pipe diameter along.

Table 4.2. Properties of the pipes (I).

Stream	Name (I)	From	to	Material	State	Flow (kg/batch)	Flow (m <sup>3</sup> /s)	Speed (m/s)	Density (kg/m <sup>3</sup> )	Viscosity (N·s/m <sup>2</sup> )	Sheet N.
1	P101-1"-SA-178A	De-water net	T-101	Deionised Water	Liquid	608	10.2·10 <sup>-3</sup>	1.83	992.2	6.53·10 <sup>-3</sup>	2
2	P102-3/8"-SA-178A	T-101	P-101	Deionised Water	Liquid	608	3.4·10 <sup>-4</sup>	2.82	971.8	1.60·10 <sup>-3</sup>	2
3	P103-3/8"-SA-178A	P-101	AT-201	Deionised Water	Liquid	608	3.4·10 <sup>-4</sup>	2.82	971.8	1.60·10 <sup>-3</sup>	2
6	P201-1/4"-SA-178A	T-102	P-201	Dow Corning	Liquid	200	1.66·10 <sup>-4</sup>	1.95	1,340.8	3.89·10 <sup>-1</sup>	3/5
7	P202-1/4"-SA-178A	P-201	AT-201	Dow Corning	Liquid	200	1.66·10 <sup>-4</sup>	2.10	1,340.8	3.89·10 <sup>-1</sup>	3/5
11	P301-3/8"-SA-178A	T-103	P-301	Pure Thix HH	Liquid	50	8.29·10 <sup>-5</sup>	2.26	1,005	3.38·10 <sup>-1</sup>	4/5
12	P302-3/8"-SA-178A	P-301	AT-201	Pure Thix HH	Liquid	50	8.29·10 <sup>-5</sup>	2.62	1,005	3.38·10 <sup>-1</sup>	4/5
13	P401-1/2"-SA-178A	AT-201	P-501	Final product	Liquid	1,000	1.99·10 <sup>-4</sup>	1.01	1,387.2	9.72·10 <sup>-2</sup>	5/5
14	P402-1/2"-SA-178A	P-501	T-104	Final product	Liquid	1,000	1.99·10 <sup>-4</sup>	1.10	1,387.2	9.72·10 <sup>-2</sup>	5/6

(1) The material of the pipe is included on the name (material: SA-178)

Table 4.2. Properties of the pipes (II).

Stream	Name	From	to	Material	P op (atm)	P des (atm)	T op (°C)	T des (°C)	D in (mm)	D out (mm)	DN (in)	Schedule	Insulation
1	P101-1"-SA-178A	De-water net	T-101	Deionised Water	1	2	17	37	26.7	33.4	1	40	Yes
2	P102-3/8"-SA-178A	T-101	P-101	Deionised Water	1	2	60	80	12.5	17.2	3/8	40	No
3	P103-3/8"-SA-178A	P-101	AT-201	Deionised Water	1	2	60	80	12.5	17.2	3/8	40	No
6	P201-1/4"-SA-178A	T-102	P-201	Dow Corning	1	2	17	37	10.4	13.7	1/4	40	No
7	P202-1/4"-SA-178A	P-201	AT-201	Dow Corning	1	2	17	37	10.4	13.7	1/4	40	No
11	P301-3/8"-SA-178A	T-103	P-301	Pure Thix HH	1	2	17	37	6.8	10.3	3/8	40	No
12	P302-3/8"-SA-178A	P-301	AT-201	Pure Thix HH	1	2	17	37	6.8	10.3	3/8	40	No
13	P401-1/2"-SA-178A	AT-201	P-501	Final product	1	2	17	37	15.80	21.3	1/2	40	No
14	P402-1/2"-SA-178A	P-501	T-104	Final product	1	2	17	37	15.80	21.3	1/2	40	No

#### **4.2.2. Description the control strategy**

The control strategy consists of the implementation of an automatic surveillance and a corrective action system with the installation of a set of instruments that allow the measuring and manipulation of the production process, constituting the control system.

The keys to process control are the controlled variables, the manipulated variables, the disturbances, and the dependent variables. The values of the controlled variables and the dependent variables depend upon the values of the manipulated variables and the disturbances. The controlled variables must be maintained at or near a target, although occasionally a range of values for one or more controlled variables is acceptable. Although targets are not provided for the dependent variables, constraints often must be considered. The values of the manipulated variables are at the discretion of the control system, but are possibly subject to constraints. The values of the disturbances are determined by factors other than the control system. To maintain each controlled variable at its target, the number of manipulated variables must, at least, equal the number of controlled variables (a “square” system). In most process applications, there are more manipulated variables than controlled variables (a “fat” system), and this creates opportunities for optimization.

The safety operation is a primary requirement to avoid accidents that may affect the staff working and even partially or completely destroy the production facility. This safety is usually tied to specific operating variables such as temperature, levels, pressures and compositions and should never exceed certain values.

The level of automation of the plant seeks an in-line optimization which acts in real-time on the points of the controlled variables, so the process is continually operating at optimal conditions. To operate at this level of automation, a computer must be programmed with the calculations based on an optimized model of the process with the role of reducing costs. In order to simplify and to determine the control strategy, a basic regulatory control and advanced regulatory control are used, where control loops are involved in cascade controls, feed forward or proportional control as detailed in each case. (ref. 9)

#### **4.2.2.1. De-water tank T-101**

The warm De-water Tank (T-101) is a cylindrical tank with plain heads. It works at atmospheric pressure and at 60 °C of temperature. The tank has an electric coil whose function is to heat the De-water, which is supplied by De-water net.

Power supply in electric coil: as mentioned before, this tank has an electric serpentine coil which heats De-water from room temperature to 60 °C. Therefore, an electric control TICA-101 has been designed, it controls the intensity of the electric coil to achieve a De-water temperature of 60 °C. The control variable is the temperature of De-water and the manipulate variable is the intensity of the electric coil. The set point was fixed at  $60 \pm 1$  °C. The temperature indicator measures the temperature of the De-water and sends the signal to the control G-101, which switches on or off depending on the set point. The switch works as an inverse direct control; at higher temperature (more than set point) the control switches off and at lower it switches on.

Flow control: the outflow is measured by FICQA-101 (Flow Indicator Control Quantity Alarm) which controls the mass amount of outflow to the tank. This control measures and totalizes the quantity of outflow. When the quantity of flow achieves the set point, the valves close.

Intensity control: as already mentioned, the tank has an electric coil which is controlled by G-101. In case of overload or failure, the CIAS-101 and CIAS-102 (Control Indicator Intensity Alarm Switch) cut off the power supply for P101A/B.

Level Control: LIA-101 (Level indicator Alarm) measures the level of the T-101 for HHL and LL. The aim is to keep the tank filled at a proper level and avoid the cavitation of the pumps P-101A/B during unloading.

#### **4.2.2.2. Storage tanks for raw material T-102 and T-103**

The storage tanks for the raw materials are cylindrical and the heads are semi elliptical. The raw materials are stored at atmospheric conditions and room temperature. They must be made inert with nitrogen to avoid the oxidation of the compounds.

The strategies control for the tanks T-102 and T-103 are the same. As follows, it is explained the control for T-102. They have the same numeration, for example instead of FCV-201 in T-103 is FCV-301.

Pressure control: the blanketing of the tank to avoid oxidation of the material is made with nitrogen. To avoid vacuum and overpressure problems during the maintenance, PICA-201 (Pressure Indicator Control Alarm) is installed, which controls input of nitrogen acting on an automatic PCV-204 and PCV-205 (control valves), inflow and outflow of nitrogen, respectively. The control variable is the pressure inside the tank and the manipulated variable is the input and output of nitrogen. PCV-204 is of inverse action; therefore, if the pressure is high the control valve PCV-204 closes. PCV-205 is of direct action; therefore, if the pressure is high the PCV-205 opens.

Flow control: the outflow is measured by FICQA-201 (Flow Indicator Control Quantify Alarm) which controls the mass amount of outflow to the tank. This control measures and totalizes the quantity of outflow. When the quantity of flow achieves the set point the valves close.

Level Control: as same as the tank T-101, it has a LIA-201 (Level Indicator Alarm) inside the tank. The aim of the LIA-201 for HHL and LL is to keep the tank filled at a certain level and avoid the cavitation of the pumps P-201A/B during unloading. During the loading procedure, the raw material enters through one inflow which has LCV-201 connected to the tank level controller with alarm and switch by LIA-201. If the level of the stored compound exceeds the safety level HL established by the company (80% volume) LCV-201 would close, preventing the entry of more material. Just before entering the tank, there is a manual valve in case that the first valve does not respond properly.

In case of low level in this tank, LIAS-201 acts manipulating FVC-202 which cuts off pumping of pumps P-201A/B during raw material unloading and closing FCV-202 to avoid the cavitation in the pumps.

At the bottom, the tank has three outputs: one output is to carry out the purge of the tank to complete drainage; the other exit is used to take samples, analyze them and determine whether the material has the required conditions, and the third output (V-202A and V-202B) goes into the agitation tank (AT-201). All these outlets are manual valves.

Temperature Control: the TI-201 (Temperature Indicator) measures the temperature of the fluid inside the tank. It sends the signal to control room. Therefore, it knows the temperature value.

Intensity control: CIIAS-201 and CIIAS-202 (Control Indicator Intensity Alarm Switch) controls the power supply for P201A/B. In case of overload or failure CIIAS-101 and CIIAS-102 cut off the power supply when the pumps P201A/B are in service.

Level Control: As already mentioned in T-101, T-102 has a LIA-201 (Level Indicator Alarm) inside the tank. The aim of LIA-201 for HHL and LL is to fill the tank with the proper level and avoid the cavitation of the pumps P-101A/B during unloading.

#### **4.2.2.3. Agitation tank AT-201**

The agitation tank AT-201 has heads semi elliptical and the body has 2 shapes. The first part is cylindrical and the second part is troncoconic with an angle of 35° to facilitate the unloading of this product which is considerate of medium viscosity.

Cooling jacket: the aim is to achieve the optimal conditions, in cooling process of the mixture from 60°C to room temperature. The control strategies used are a cascade control temperature-temperature-flow. In cascade loop, the variable controlled is the temperature of the mixture in the agitation tank AT-201 and the order variable is the inflow of water cooling. The action is direct; therefore, at higher temperature of mixture it requires more cooling water flow. TICA-501 (Temperature Indicator Control Alarm) acts on the TICA-502, which corrects the flow in the cooling water, according to the temperature of the mixture. The temperature of mixture is controlled by TICA-501 whose set point is fixed at  $17 \pm 1^\circ\text{C}$ , when cooling process starts. The transmitter of temperature sends the value temperature to TICA-502. In function of this temperature and the temperature of cooling water a signal is send to the inflow of cooling water by flow control FICA-505.

Control Ratio: the aim to control the Ratio control is to ensure that two or more process variables, such as one raw material flow, are kept at the same ratio even if they are changing in value. In this case, it keeps the relation between the raw compounds which are stored in tanks: De-water, Dow Corning and Pure Thix HH.

The agitation tank AT-201 has 2 ratio loops. The first one, FICQA-502 needs a set point from R-501, according to the quantity of flow measures by FICQA-501. It uses the signal from flow transmitter. An adjustable fraction of this signal is used as a set point so that the controller manipulates the FCV-502 to hold the two flows achieve this ratio. The second loop is exactly the same as the first one; with the other set point at R-502. The set points are fixed according to the sunscreen recipe.

Intensity control and flow control: as the same as others tanks, this tank has CIAS-501 and CIAS-502 (Control Indicator Intensity Alarm Switch) which control the power supply for P501A/B. In case of overload or failure CIAS-501 and CIAS-502 cut off the energy supply. The inflow is controlled by FICQA-501, FICQA-502 and FICQA-503, as stated before, in Ratio control. FICQA-504 controls and quantifies the outflow of the agitation tank.

#### **4.2.2.4. Final product tank T-104**

The final product tank (T-104) is a cylindrical tank with plain heads. It works at atmospheric pressure and room temperature.

Temperature and level indicator: the TI-401 (Temperature Indicator) and LIA 401 measure the temperature and the level of the fluid inside the tank, respectively, and the signal is sent to control room.

Pressure control: the pressure control is the same as tanks T-102 and T-103. The blanketing of the tank to avoid oxidation of the compound is made with nitrogen. For more details see section 4.2.2.2 of this chapter.

#### **4.2.2.5. Relation of controllers**

Table 4.3 shows the relation between the controllers and the main characteristics of each other in whole plant inside battery limits.

Table 4.3. Relations strategic controls and control.

Equipment	Name	Controlled variable	Manipulated variable	Element	Action	Failure	SP	Control
T-101	LIA-101	Liquid level T-101	Inflow T-101	LCV-101	Direct	Closed	75%	PID
		Liquid level T-101	Pump outflow P-101A/B	M-101A/B	Direct	Open	10%	PI
	TICA-101	Liquid temperature T-101	Electric power supply in coil	G-101	Inverse	Closed	60°C	PID
	CIAS-103	Generator intensity G-101	Electric power supply in coil	G-101	Inverse	Closed	*	PI
	CIAS-101	Motor intensity P-101A	Electric power supply in P-101A	M-101A	Inverse	Closed	*	PI
	CIAS-102	Motor intensity P-101B	Electric power supply in P-101B	M-101B	Inverse	Closed	*	PI
FIQA-101		Outflow T-101	Outflow T-101	FCV-102	Inverse	Open	608 kg/batch	PID
	LIA-201	Liquid level T-102	Pump outflow P-201A/B	M-201A/B	Direct	Open	10%	PID
T-102			Inflow T-102	FCV-201	Direct	Closed	80%	PI
	PICA-201	Pressure T-102	N2 inflow T-102	FCV-204	Inverse	Open	1.3 bar	PI
	PICA-201	Pressure T-102	N2 outflow T-102	FCV-205	Direct	Open	1.3 bar	PI
	FIQA-202	Dow coming outflow T-102	Outflow T-102	FCV-202	Direct	Closed	200 kg/batch	PID
	CIAS-201	Motor intensity P-201A	Electric power supply in P-201A	M-201A	Inverse	Closed	*	PID
	CIAS-202	Motor intensity P-201B	Electric power supply in P-201B	M-201B	Inverse	Closed	*	PID
T-103	LIA-301	Liquid level T-103	Pump outflow P-301A/B	M-301A/B	Direct	Open	10%	PID
			Inflow T-103	FCV-301	Direct	Closed	**	PI
	PICA-301	Pressure T-103	N <sub>2</sub> inflow T-103	FCV-304	Inverse	Closed	1.3 bar	PI
	PICA-301	Pressure T-103	N <sub>2</sub> outflow T-103	FCV-305	Direct	Open	1.3 bar	PI
	FIQA-303	Pure Thix HH outflow T-103	Outflow T-103	FCV-302	Direct	Closed	50 kg/batch	PID
	CIAS-301	Motor intensity P-301A	Electric power supply in P-301A	M-301A	Inverse	Closed	*	PID
CIAS-302		Motor intensity P-301B	Electric power supply in P-301B	M-301B	Inverse	Closed	*	PID
	LIA-501	Liquid level AT-201	Final product outflow AT-201	FCV-505	Direct	Open	1,000 kg/batch	PID
AT-201			Pump outflow P-201A/B	M-201A/B	Direct	Closed	5%	PID
	FIQA-101	De-water HH inflow AT-201	De-water HH inflow AT-201	FCV-101	Direct	Closed	608 kg/batch	PID
	FIQA-501	De-water HH inflow AT-201	De-water HH inflow AT-201	FCV-501	Direct	Closed	608 kg/batch	PID
	FIQA-502	Dow coming inflow AT-201	Dow coming inflow AT-201	FCV-502	Direct	Closed	200 kg/batch	PID
	FIQA-503	Pure Thix HH inflow AT-201	Pure Thix HH inflow AT-201	FCV-503	Direct	Closed	50 kg/batch	PID
	R-501	De-water HH inflow AT-201	Dow coming inflow AT-201	FCV-502	Direct	Closed	3.04	PID
	R502	Dow coming inflow AT-201	Pure Thix HH inflow AT-201	FCV-503	Direct	Closed	4	PID
	TICA-501	Liquid temperature AT-201	Inflow cooling water AT-201	FCV-505	Direct	Open	17 °C	PID
	TICA-502	Cooling water temperature AT-201	Inflow cooling water AT-201	FCV-505	Inverse	Open	17 °C	PID
	JIC-501	Mixer Speed AT-201	Mixer Speed AT-201	M-501	Direct	Closed	500/700	PID
	CIAS-501	Motor intensity P-501A	Electric power supply in P-501A	M-501A	Inverse	Closed	*	PID
	CIAS-502	Motor intensity P-501B	Electric power supply in P-501B	M-501B	Inverse	Closed	*	PID
	FIQA-505	Final product outflow AT-201	Final product outflow AT-201	FCV-503	Direct	Open	1,000 kg/batch	PID

\*Specify by manufacturer; \*\*It does not included in Battery limit

#### 4.2.2.6. Relation of signals and instruments

Table 4.4 shows the signals and types of flow meters, temperature, intensity, level and pressure for the transmitters installed in the plant.

Table.4.4. Signals and instruments.

Measurable variable	Description	Type meter	Type signal
Flow	Mass flow of process liquid	Micro motion	Analogical
	Mass flow of cooling water	Orifice Plate	Analogical
Temperature	Temperature liquid in tanks	Thermocouple	Analogical
Pressure	Pressure in tanks	Manometer	Analogical
Intensity	Intensity motors	Ammeter	Digital
Level	Level liquid in tanks	“Float”	Analogical
Level	Alarm HHL, LL	-	Analogical

#### 4.2.3. Equipment design

##### 4.2.3.1. Tanks

Tank T-101 is an electric serpentine coil tank whose function is to heat the deionised water supplied by deionised net. The calculations for this tank can be found in appendix 3.

Tanks T-102, T-103 and T-104 are storage tanks. T-102 and T-103 are for raw materials and T-104 is for the final product. The calculations for these tanks can be seen in appendix 3.

Table 4.4. Volume and storage capacity.

Tank	Volume (m <sup>3</sup> )	Storage capacity	N° batch/month
<b>T-101</b>	1.0	Kg/Batch	-
<b>T-102</b>	25.1	1 monthly	120
<b>T-103</b>	7.6	1 monthly	120
<b>T-104</b>	122.0	1 monthly	120

Table 4.4 shows the main criteria which have been followed to design these tanks. Concretely, it shows the criteria to choose the volume of the tanks according to production schedule.

**4.2.3.2. Agitation tank AT-201**

The agitation tank is a mixer vessel of 1.1 m<sup>3</sup> of capacity. This agitation impeller has a mixer which operates at a different speed according to the recipe to elaborate the emulsion. This tank is supported by a metallic structure 1 m of high, which consists of 4 equidistant legs.

Agitator design: The impeller has a 2-paddles configuration. This impeller has 6-paddles located at 0.2 m between each other along the shaft. The diameter of impeller is 0.7D of the agitation tank. These paddles generate currents in a radial and tangential direction to the axis of the impeller.

Vessel Design: This agitator tank has a semielliptic and open head. The body has two geometries: the top is a cylinder and H~D. The bottom is troncoconic with an angle of 35° to facilitate the unloading of this product which is considered of medium viscosity. All the characteristics are in his specification sheet. This agitator tank has 4 equidistant baffles located inside the tank. Baffles help the impeller to form the mixing pattern. They are installed vertically along the wall side on the cylindrical part of the tank. (ref. 10 - 11).

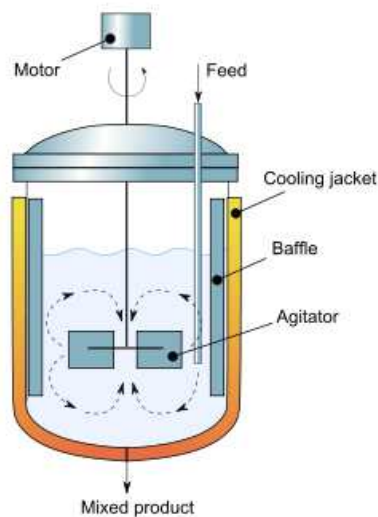


Figure 4.3. Simple sketch of the agitation vessel.

Table 4.5 Characteristics of the mixer.

<b>Number of Paddles</b>	6
<b>Space between Paddles (m)</b>	0.2
<b>Diameter of impeller (m)</b>	0.7
<b>Thickness of the paddle (m)</b>	0.10

- Cooling jacket design: The necessities of the process required a cooling procedure for the agitator tank; therefore a jacket was designed to achieve the temperature. The process starts at 60 °C and finishes at room temperature (17 °C). In order to achieve the final temperature, the flow of cooling water is calculated by energy balance. The most important parameters related to the design of the cooling jacket are shown in table 4.6.

Table 4.6. Characteristics of the cooling jacket.

<b>Area (m<sup>2</sup>)</b>	0.38
<b>Diameter (m)</b>	0.20
<b>Cooling water flow (kg/s)</b>	0.25

Appendix 3 shows the calculus procedure and all the parameters involved in the energy balance of the cooling jacket of the agitation tank.

#### 4.2.3.3. Pumps

In order to design the pumps is necessary to know the operating conditions, besides the initial and final pressures, available liquid column height at the suction side, drop pressure between the supply equipment and the agitation tank, as well as, temperature variations that may affect the density of the fluid and, consequently, the available column height.

Following considerations have been taken into account to calculate the mechanic balance properly:

- Fixed nominal diameters allow speeds between 1-3 m/s, trying to fix lower speed in suction than impulsion speed.
- Pipe length is calculated taking into account Australian Dangerous Goods code (ADG). This code provides minimal distances between storage tanks and process equipment. This code it is similar to ITC MIE-APQ1.
- The column fluid heights in the tanks T-101, T-102, T-103, T-104 and T-105 are considered in the most unfavourable conditions, when the pumps should do much work.

Finally, we concluded the plant has 4 pumps according to the battery limits, each one installed after each tank (T-101, T-102, T-103, and agitation tank AT-201). There is one pipe to supply

the deionised water from the water net which is a centrifuged pump. All the other pumps are membrane type because of the viscosity of the products. In appendix 2 the calculations are shown.

#### **4.2.1.3. Specification Sheets**

In this chapter is shown the specification sheets for the equipments.

➤ Specification Data for P101 A/B

1	Nº OF PUMPS	2	RUN:	SPARE:	<p style="text-align: center;"><b>SKETCH</b></p> <p>CM1-2 3" 348 V, 50 Hz Liq. bombeado = Agua Temp. del líquido = 20 °C Densidad = 998.2 kg/m³</p>	
2	SERVICE	Drive to A.T-201				
3	COM PANY	GRUNFOS				
4	MODEL	CM 1-2				
5	MAT'L PUMPED	DE-Water				
6	OPER. TEMP	60				
7	DENSITY	971,8				
8	VISCOSITY	0,0035				
9	VAPOR PRESS.(abs.)					
10	NORM.CAPACITY	0,0010				
11	EXCESS CAPACITY					
12	MAX.CAPACITY	0,0012				
13						
14	<b>SUCTION CONDITIONS</b>					
15						
16	SUCTION HEIGHT	0,25				
17	PR.AT EQUIPM.(abs.)	1				
18	HL LINE	1,03				
19	HL TOTAL	1,1				
20	NPSH (m.w.c.)	6,95				
21						
22	<b>DISCHARGE CONDITIONS</b>					
23	LIQUID HEAD	2				
24	PR. AT EQUIPM.(abs.)	1,17				
25	HL LINE					
26	EQUIP.PR.DROP					
27	EQUIP.PR.DROP					
28	EQUIP.PR.DROP					
29	EQUIP.PR.DROP					
30	HL FRICTION	0,5				
31	HL TOTAL	0,9				
32	H PUMP	14,3				
33	TOTAL DISC PRESSURE	1,2				
34	<b>PUMP REQUIREMENTS</b>					
35	TYPE PUMP	centrifugal		<b>SUCTION</b>	<b>DISCHARGE</b>	
36	ESTIMATED EFF.	56,8		LINE SIZE	3/8in	
37	ESTIMATED Rot.freq.	s-1		HORIZON,RUN	3 m	
38	ESTIMATED Power	0,5 kW		VERT,RUN	0,8 m	
39	TYPE DRIVER			ELBOW L.R.	PCS 2	
40	STEAM (abs.)	bar		ELBOW M.R.	PCS	
41	EXHAUST (abs.)	bar		CHECK VALVE	PCS 1	
42	ELECTRICITY	V:	PH: 50	BALL VALVE	PCS 1	
43	ENCLOSURE			GATE VALVE	PCS 2	
44				PLUG VALVE	PCS	
45				GLOBE VALVE	PCS	
46				DIAPHR. VALVE	PCS	
47	<b>PUMP MATERIALS</b>			CONTR. VALVE	PCS 1	
48	CASE			STRAINER	PCS	
49	IMPELLER	GG25		TEE	PCS	
50	SHAFT	F124		OTHERS		
51	SHAFT SLEEVE	316L		TOTAL	1,31 m	
52	SEAL/PACKING	Simple		TOTAL	2 m	
53	GASKETS			Name P102-3/8"SA -178A	Name P103-3/8"SA -178A	
54	GEAR			LINE PRESSURE DROP	bar	
55	PISTON					
	JOB NO.	CHARGE NO.		<p><b>P-101 A/B</b></p> <p><b>UNIVERSITAT ROVIRA I VIRGILI</b> Escola Tècnica Superior d'Enginyeria Química Departament d'Enginyeria Química</p>		
	M/S NO.	P.O.NO.				
	NO.UNITS					
	DR.BY	DATE:				
	CK.BY	DATE:				
	REV	BY	DATE			
			11/05/2012			
	SHEET No.	1				

➤ Specification Data for P201 A/B

1	Nº OF PUMPS	2	RUN:	SPARE:	<p style="text-align: center;"><b>SKETCH</b></p>			
2	SERVICE	Drive to AT-201						
3	COMPANY	GRUNFOS						
4								
5	MAT'L PUMPED	Dow Corning						
6	OPER. TEMP	17	°C					
7	DENSITY	1374,8	kg/m3					
8	VISCOSITY	0,3900	Pa.s					
9	VAPOR PRESS.(abs.)		bar					
10	NORM. CAPACITY	0,0002	m3/s					
11	EXCESS CAPACITY		m3/s					
12	MAX. CAPACITY	0,00024	m3/s					
13								
14	<b>SUCTION CONDITIONS</b>							
15								
16	SUCTION HEIGHT	0,25	m					
17	PR. AT EQUIPM.(abs.)	1	bar					
18	HL LINE	1,04	m					
19	HL TOTAL	1,1	bar					
20	NPSH (m.w.c.)		m					
21								
22	<b>DISCHARGE CONDITIONS</b>							
23	LIQUID HEAD	1,5	m					
24	PR. AT EQUIPM.(abs.)	1,17	bar					
25	HL LINE	2,4	m					
26	EQUIP. PR. DROP		bar					
27	EQUIP. PR. DROP		bar					
28	EQUIP. PR. DROP		bar					
29	EQUIP. PR. DROP		bar					
30	HL FRICTION	0,9	bar					
31	HL TOTAL	1,7	m					
32	H.PUMP		m					
33	TOTAL DISC PRESSURE	1,4	bar					
34	<b>PUMP REQUIREMENTS</b>				<b>SUCTION</b>	<b>DISCHARGE</b>		
35	TYPE PUMP	Membrane		LINE SIZE	1/4in	LINE SIZE	1/4in	
36	ESTIMATED EFF.			HORIZON,RUN	3 m	HORIZON,RUN	4 m	
37	ESTIMATED Rot.freq.	s-1		VERT,RUN	1,0 m	VERT,RUN	2 m	
38	ESTIMATED Power	1,9 kW		ELBOW L.R.	PCS 2	ELBOW L.R.	PCS 2	
39	TYPE DRIVER			ELBOW M.R.	PCS	ELBOW M.R.	PCS	
40	STEAM (abs.)	bar	°C	CHECK VALVE	PCS	CHECK VALVE	PCS 1	
41	EXHAUST (abs.)	bar	°C	BALL VALVE	PCS	BALL VALVE	PCS 1	
42	ELECTRICITY	V:	Hz	GATE VALVE	PCS 2	GATE VALVE	PCS 2	
43	ENCLOSURE			PLUG VALVE	PCS	PLUG VALVE	PCS	
44				GLOBE VALVE	PCS	GLOBE VALVE	PCS	
45				DIAPHR. VALVE	PCS	DIAPHR. VALVE	PCS	
46	<b>PUMP MATERIALS</b>				CONTR. VALVE	PCS	CONTR. VALVE	PCS 1
47	CASE	SA 285		STRAINER	PCS	STRAINER	PCS	
48	IMPELLER			TEE	PCS	TEE	PCS	
49	SHAFT			OTHERS		OTHERS		
50	SHAFT SLEEVE			TOTAL	2,26 m	TOTAL	1,4 m	
51	SEAL/PACKING							
52	GASKETS			Name P201-1/4\"SA-178A		Name P202-1/4\"SA-178A		
53	GEAR			LINE PRESSURE DROP	bar	LINE PRESSURE DROP	bar	
54	PISTON							
55								
JOB NO.		CHARGE NO.		<p><b>P-201 A/B</b></p>				
M/S NO.		P.O.NO.						
NO.UNITS								
DR.BY		DATE:						
CK.BY		DATE:						
REV	BY	DATE		<p><b>UNIVERSITAT ROVIRA I VIRGILI</b> Escola Tècnica Superior d'Enginyeria Química Departament d'Enginyeria Química</p>				
		11/05/2012						
SHEET No.		2						

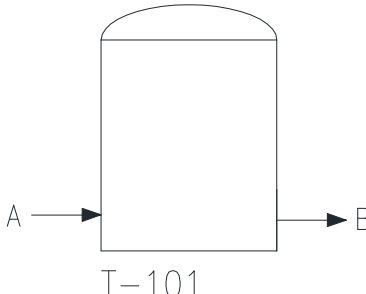


➤ Specification Data for P301 A/B

1	Nº OF PUMPS	2	RUN:	SPARE:	<p style="text-align: center;"><b>SKETCH</b></p>			
2	SERVICE	Drive to AT-201						
3	COMPANY		GRUNFOS					
4								
5	MATL PUMPED		Pure Thix HH					
6	OPER. TEMP		17	°C				
7	DENSITY		1005	kg/m3				
8	VISCOSITY		0,1380	Pa.s				
9	VAPOR PRESS.(abs.)			bar				
10	NORM.CAPACITY		0,00008	m3/s				
11	EXCESS CAPACITY			m3/s				
12	MAX.CAPACITY		0,0001	m3/s				
13								
14	<b>SUCTION CONDITIONS</b>							
15								
16	SUCTION HEIGHT		0,25	m				
17	PR. AT EQUIPM.(abs.)		1	bar				
18	HL LINE		0,8	m				
19	HL TOTAL		1	bar				
20	NPSH (m.w.c.)			m				
21								
22	<b>DISCHARGE CONDITIONS</b>							
23	LIQUID HEAD		1,5	m				
24	PR. AT EQUIM.(abs.)		1,17	bar				
25	HL LINE		2,4	m				
26	EQUIP.PR.DROP		1,09	bar				
27	EQUIP.PR.DROP			bar				
28	EQUIP.PR.DROP			bar				
29	EQUIP.PR.DROP			bar				
30	HL FRICTION		0,5	m				
31	HL TOTAL		0,8	m				
32	H PUMP			m				
33	TOTAL DISC PRESSURE		1,3	bar				
34	<b>PUMP REQUIREMENTS</b>				<b>SUCTION</b>	<b>DISCHARGE</b>		
35	TYPE PUMP		Membrane	LINE SIZE	1/8in	LINE SIZE	1/8in	
36	ESTIMATED EFF.			HORIZON.RUN	3 m	HORIZON.RUN	4 m	
37	ESTIMATED Rot.freq.			VERT.RUN	1,0 m	VERT.RUN	2 m	
38	ESTIMATED Power		0,4 kW	ELBOW L.R.	PCS 2	ELBOW L.R.	PCS 2	
39	TYPE DRIVER			ELBOW M.R.	PCS	ELBOW M.R.	PCS	
40	STEAM (abs.)		bar	°C	CHECK VALVE	PCS	CHECK VALVE	PCS 1
41	EXHAUST (abs.)		bar	°C	BALL VALVE	PCS	BALL VALVE	PCS 1
42	ELECTRICITY	V:	PH:	50 Hz	GATE VALVE	PCS 2	GATE VALVE	PCS 2
43	ENCLOSURE				PLUG VALVE	PCS	PLUG VALVE	PCS
44					GLOBE VALVE	PCS	GLOBE VALVE	PCS
45					DIAPHR. VALVE	PCS	DIAPHR. VALVE	PCS
46	<b>PUMP MATERIALS</b>				CONTR. VALVE	PCS	CONTR. VALVE	PCS 1
47	CASE				STRAINER	PCS	STRAINER	PCS
48	IMPELLER				TEE	PCS	TEE	PCS
49	SHAFT				OTHERS		OTHERS	
50	SHAFT SLEEVE				TOTAL	2,15 m	TOTAL	1,3 m
51	SEAL/PACKING							
52	GASKETS				Name	P302-1/8\"SA-178A	Name	P302-1/8\"SA-178A
53	GEAR				LINE PRESSURE DROP	bar	LINE PRESSURE DROP	bar
54	PISTON							
55								
	JOB NO.		CHARGE NO.		<b>P-301 A/B</b>		<b>SolarOz</b> Skin care	
	M/S NO.		P.O.NO.					
	NO. UNITS							
	DR. BY		DATE:					
	CK. BY		DATE:					
	REV		BY		<p><b>UNIVERSITAT ROVIRA I VIRGILI</b> Escola Tècnica Superior d'Enginyeria Química Departament d'Enginyeria Química</p>			
			DATE					
			11/05/2012					
	SHEET No.		3					



➤ Specification Data for P501 A/B

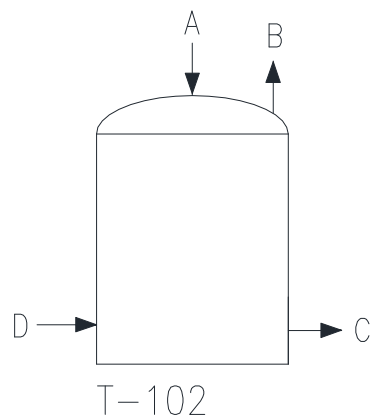
1	NP OF PUMPS	2	RUN:	SPARE:	<p style="text-align: center;"><b>SKETCH</b></p>
2	SERVICE	Drive to T-104			
3	COMPANY		GRUNFOS		
4					
5	MATL PUMPED		Final product		
6	OPER. TEMP		17	°C	
7	DENSITY		1387	kg/m3	
8	VISCOSITY		0,0970	Pa.s	
9	VAPOR PRESS.(abs.)			bar	
10	NORM. CAPACITY		0,0004	m3/s	
11	EXCESS CAPACITY			m3/s	
12	MAX. CAPACITY		0,00048	m3/s	
13					
14	<b>SUCTION CONDITIONS</b>				
15					
16	SUCTION HEIGHT		0,25	m	
17	PR. AT EQUIPM.(abs.)		1	bar	
18	HL. LINE		1,03	m	
19	HL. TOTAL		1	bar	
20	NPSH (m.w.c.)			m	
21					
22	<b>DISCHARGE CONDITIONS</b>				
23	LIQUID HEAD		1,5	m	
24	PR. AT EQUIPM.(abs.)		1,27	bar	
25	HL. LINE		1,1	m	
26	EQUIP. PR. DROP			bar	
27	EQUIP. PR. DROP			bar	
28	EQUIP. PR. DROP			bar	
29	EQUIP. PR. DROP			bar	
30	HL. FRICTION		0,5	m	
31	HL. TOTAL		0,9	m	
32	H PUMP			m	
33	TOTAL DISC PRESSURE		1,2	bar	
34	<b>PUMP REQUIREMENTS</b>				
35	TYPE PUMP		Membrane		
36	ESTIMATED EFF.				
37	ESTIMATED Rot.freq.		s-1		
38	ESTIMATED Power		1,82	kW	
39	TYPE DRIVER				
40	STEAM (abs.)		bar	°C	
41	EXHAUST (abs.)		bar	°C	
42	ELECTRICITY	V:	PH:	50 Hz	
43	ENCLOSURE				
44					
45					
46	<b>PUMP MATERIALS</b>				
47	CASE				
48	IMPELLER				
49	SHAFT				
50	SHAFT SLEEVE				
51	SEAL/PACKING				
52	GASKETS				
53	GEAR				
54	PISTON				
55					
JOB NO.		CHARGE NO.		<p><b>P-501 A/B</b></p>	
M/S NO.		P.O.NO.			
NO. UNITS					
DR. BY		DATE:			
CK. BY		DATE:			
REV	BY	DATE		<p><b>UNIVERSITAT ROVIRA I VIRGILI</b> Escola Tècnica Superior d'Enginyeria Química Departament d'Enginyeria Química</p>	
		11/05/2012			
SHEET No.		4			

➤ Specification Data for T-101

1	GENERAL		Item: T-101		SKETCH  
2	GENERAL		Service:		
3	GENERAL		Type of supports: Cimentation		
4	GENERAL		Capacity: 1.1 m <sup>3</sup> Diameter: 1 m High: 1.1m		
5	OPER. COND.		Operating Pressure	1 bar	
6	OPER. COND.		Operating Temperature	60 °C	
7	OPER. COND.		Liquid Density	972 kg/m <sup>3</sup>	
8	OPER. COND.		Inlet flow	m3/h	
9	OPER. COND.		Outlet flow	m3/h	
10	DESIGN DATA		Design Pressure (eff.)	2 bar	
11	DESIGN DATA		MAWP	2 bar	
12	DESIGN DATA		Design Temperature	80 °C	
13	DESIGN DATA		Corr. Allow.	3 mm	
14	DESIGN DATA		Courses:	Nº	
15	DESIGN DATA		Joint Eff.		
16	DESIGN DATA		Code:	ASME	
17	DESIGN DATA		Radiograph:	85 %	
18	DESIGN DATA		Stress Relieve:	<input type="checkbox"/> Yes Parts:	
19	DESIGN DATA		Insulation:	<input type="checkbox"/> No thick mm.	
20	DESIGN DATA		Fireproofing:	<input checked="" type="checkbox"/> No	
21	DESIGN DATA		Paint:	<input checked="" type="checkbox"/> Yes Parts:	
22	DESIGN DATA			<input type="checkbox"/> No	
23	DESIGN DATA		Wt. Empty:	1719 N	
24	DESIGN DATA		Wt. Full of product:	11200 N	
25	DESIGN DATA		Wt. Full of water:	kg	
26	DESIGN DATA		Hydrostatic Test (eff.)	2.6 bar	
27	MATERIALS		Thick. (mm)	Mat'l Class	
28	MATERIALS		Roof	5 SA-283A	
29	MATERIALS		Shell course	7 SA-283A	
30	MATERIALS		8		
31	MATERIALS		7		
32	MATERIALS		6		
33	MATERIALS		5		
34	MATERIALS		4		
35	MATERIALS		3		
36	MATERIALS		2		
37	MATERIALS		1		
38	MATERIALS		Bottom	5 SA-283A	
39	MATERIALS		Perimetral ring		
40	NOZZLES		Service	Mark No. Dia. Rating	
41	NOZZLES		De-Water inflow	A	
42	NOZZLES		De-Water outflow	B	
43	NOZZLES			C	
44	NOZZLES			D	
45	NOZZLES			E	
46	NOZZLES			F	
47	NOZZLES			G	
48	NOZZLES			H	
49	NOZZLES			I	
50	NOZZLES			J	
51	NOZZLES			K	
52	NOZZLES			L	
53	NOZZLES			M	
54	NOZZLES			N	
55	NOTES:				
56			Sheet Nr.		T-101 
57			6		
58					
59					
60					
					 UNIVERSITAT ROVIRA I VIRGILI Escola Tècnica Superior d'Enginyeria Química Departament d'Enginyeria Química
0	Specification T-101	11/05/2012	P. Corbi	P. Corbi	
REV.	DESCRIPTION	DATE	PREP.	APPR.	

➤ Specification Data for T-102

1	GENERAL	Item: T-102					
2		Service:					
3		Type of supports: Cimentation					
4		Capacity: 25.1 m <sup>3</sup> Diameter: 3.5 m High: 4.7m					
5	OPER. COND.	Operating Pressure	1	bar			
6		Operating Temperature	17	°C			
7		Liquid Density	1370	kg/m <sup>3</sup>			
8		Inlet flow		m <sup>3</sup> /h			
9		Outlet flow		m <sup>3</sup> /h			
10	DESIGN DATA	Design Pressure (eff.)	2	bar			
11		MAWP	2	bar			
12		Design Temperature	37	°C			
13		Corr. Allow.	3	mm			
14		Courses:		Nº			
15		Joint Eff.					
16		Code:	ASME				
17		Radiograph:	85	%			
18		Stress Relieve:	<input type="checkbox"/> Yes	Parts:			
19			<input type="checkbox"/> No				
19		Insulation:	<input type="checkbox"/> Yes	thick mm.			
20		<input checked="" type="checkbox"/> No					
20	Fireproofing:	<input type="checkbox"/> Yes					
21		<input checked="" type="checkbox"/> No					
22	Paint:	<input checked="" type="checkbox"/> Yes	Parts:				
22		<input type="checkbox"/> No					
23	Wt. Empty:	26037	N				
24	Wt. Full of product:	4·10 <sup>5</sup>	N				
25	Wt. Full of water:		kg				
26	Hydrostatic Test (eff.)	2.6	bar				
27	MATERIALS		Thick. (mm)	Mat'l Class			
28		Roof	7	SA-283A			
29		Shell course	8	SA-283A			
30		8					
31		7					
32		6					
33		5					
34		4					
35		3					
36		2					
37	1						
38	Bottom	8	SA-283A				
39	Perimetral ring						
40	NOZZLES	Service	Mark	No.	Dia.	Rating	
41		Nitrogen inflow	A				
42		Nitrogen outflow	B				
43		Dow Corning outflow	C				
44		Dow Corning inflow	D				
45			E				
46			F				
47			G				
48			H				
49			I				
50			J				
51			K				
52			L				
53			M				
54			N				
55	NOTES:				Sheet Nr. 7	T-102	
56							
57							
58							
59						UNIVERSITAT ROVIRA I VIRGILI Escola Tècnica Superior d'Enginyeria Química Departament d'Enginyeria Química	
0	Specification T-102	11/05/2012	P. Corbi	P. Corbi			
REV.	DESCRIPTION	DATE	PREP.	APPR.			



➤ Specification Data for T-103

1	GENERAL		Item: T-103		<p style="text-align: center;">SKETCH</p>			
2	Service:							
3	Type of supports: Cimentation							
4	Capacity: 7.6 m <sup>3</sup> Diameter: 1.6 m High: 3.5m							
5	OPER. COND.	Operating Pressure	1	bar				
6		Operating Temperature	17	°C				
7		Liquid Density	1005	kg/m <sup>3</sup>				
8		Inlet flow		m <sup>3</sup> /h				
9		Outlet flow		m <sup>3</sup> /h				
10	DESIGN DATA	Design Pressure (eff.)	2	bar				
11		MAWP	2	bar				
12		Design Temperature	37	°C				
13		Corr. Allow.	3	mm				
14		Courses:		Nº				
15		Joint Eff.						
16		Code:	ASME					
17		Radiograph:	85	%				
18		Stress Relieve:	<input type="checkbox"/> Yes	Parts:				
19		Insulation:	<input type="checkbox"/> No	thick mm.				
20	Fireproofing:	<input checked="" type="checkbox"/> Yes						
21		<input checked="" type="checkbox"/> No						
22	Paint:	<input checked="" type="checkbox"/> Yes	Parts:					
23		<input type="checkbox"/> No						
24	Wt. Empty:	9249	N					
25	Wt. Full of product:	83838	N					
26	Wt. Full of water:		kg					
27	Hydrostatic Test (eff.)	2.6	bar					
28	MATERIALS		Thick. (mm)	Mat'l Class				
29		Roof	6	SA-283A				
30		Shell course	7	SA-283A				
31		8						
32		7						
33		6						
34		5						
35		4						
36		2						
37	1							
38	Bottom	6	SA-283A					
39	Perimetral ring							
40	NOZZLES	Service	Mark	No.	Dia.	Rating		
41		Nitrogen inflow	A					
42		Nitrogen outflow	B					
43		Thix HH outflow	C					
44		Thix HH inflow	D					
45			E					
46			F					
47			G					
48			H					
49			I					
50			J					
51			K					
52			L					
53			M					
54			N					
55	NOTES:					Sheet Nr. 8	T-103	
56								
57							UNIVERSITAT ROVIRA I VIRGILI Escola Tècnica Superior d'Enginyeria Química Departament d'Enginyeria Química	
58	0	Specification T-103	11/05/2012	P. Corbí	P. Corbí			
59	REV.	DESCRIPTION	DATE	PREP.	APPR.			

➤ Specification Data for AT-201

1	GENERAL		Item: AT-201		<p style="text-align: center;">SKETCH</p>			
2			Service:					
3			Type of supports: Legs					
4			Capacity: 1.1 m <sup>3</sup> Diameter: 1 m High: 1.1m					
5	OPER. COND.		Operating Pressure	1 bar				
6			Operating Temperature	60 °C				
7			Liquid Density	1376 kg/m <sup>3</sup>				
8			Inlet flow	m <sup>3</sup> /h				
9			Outlet flow	m <sup>3</sup> /h				
10	DESIGN DATA		Design Pressure (eff.)	2 bar				
11			MAWP	2 bar				
12			Design Temperature	80 °C				
13			Corr. Allow.	3 mm				
14			Courses:	Nº				
15			Joint Eff.					
16			Code:	ASME				
17			Radiograph:	85 %				
18			Stress Relieve:	<input type="checkbox"/> Yes <input type="checkbox"/> No	Parts:			
19			Insulation:	<input type="checkbox"/> Yes <input checked="" type="checkbox"/> No	thick mm.			
20	Fireproofing:	<input type="checkbox"/> Yes <input checked="" type="checkbox"/> No						
22	Paint:	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No	Parts:					
23	Wt. Empty:	409951 N						
24	Wt. Full of product:	424868 N						
25	Wt. Full of water:	kg						
26	Hidrostatic Test (eff.)	2.6 bar						
27			Thick. (mm)	Mat'l Class				
28	Roof	5		SA-283A				
29	Shell (cylindre/troconic)	7 / 10		SA-283A				
30	8							
31	7							
32	6							
33	5							
34	4							
35	3							
36	2							
37	1							
38	Bottom	4		SA-283A				
39	Perimetral ring							
40			Service	Mark	No.	Dia.	Rating	
41	NOZZLES		Deionezed w ater	A				
42			Dow Corning	B				
43			Pure Thix HH	C				
44			Laponite XLG	D				
45			Gel w hite L	E				
46			Opigel VXX	F				
47			Citric Acid	G				
48			Titanium Dioxide	H				
49			Glycerine	I				
50			Dow icil 200	J				
51			Final Product	K				
52				L				
53				M				
54				N				
55	NOTES:				Sheet Nr.		AT-201	
56					9			
57								
58								
59								
0	Specification AT-201	11/05/2012	P. Corbi	P. Corbi				
REV.	DESCRIPTION	DATE	PREP.	APPR.				

➤ Specification Data for T-104

1	GENERAL		Item: T-104		<p>SKETCH</p>		
2	Service:						
3	Type of supports: Cimentation						
4	Capacity: 122 m <sup>3</sup> Diameter: 4.2 m High: 8.1m						
5	OPER. COND.	Operating Pressure	1	bar			
6		Operating Temperature	17	°C			
7		Liquid Density	1387	kg/m <sup>3</sup>			
8		Inlet flow		m <sup>3</sup> /h			
9		Outlet flow		m <sup>3</sup> /h			
10	DESIGN DATA	Design Pressure (eff.)	2	bar			
11		MAWP	2	bar			
12		Design Temperature	37	°C			
13		Corr. Allow.	3	mm			
14		Courses:		Nº			
15		Joint Eff.					
16		Code:	ASME				
17		Radiograph:	85	%			
18		Stress Relieve:	<input type="checkbox"/> Yes	Parts:			
			<input type="checkbox"/> No				
19		Insulation:	<input type="checkbox"/> Yes	thick mm.			
			<input checked="" type="checkbox"/> No				
20		Fireproofing:	<input type="checkbox"/> Yes				
			<input checked="" type="checkbox"/> No				
22	Paint:	<input checked="" type="checkbox"/> Yes	Parts:				
		<input type="checkbox"/> No					
23	Wt. Empty:	126287	N				
24	Wt. Full of product:	1788136	N				
25	Wt. Full of water:		kg				
26	Hydrostatic Test (eff.)	2.6	bar				
27	MATERIALS		Thick. (mm)	Mat'l Class			
28		Roof	10	SA-283A			
29		Shell course	12	SA-283A			
30		8					
31		7					
32		6					
33		5					
34		4					
35		3					
36		2					
37	1						
38	Bottom	12	SA-283A				
39	Perimetral ring						
40	NOZZLES	Service	Mark	No.		Dia.	Rating
41		Nitrogen inflow	A				
42		Nitrogen outflow	B				
43		Final product outflow	C				
44		Final product inflow	D				
45			E				
46			F				
47			G				
48			H				
49			I				
50			J				
51			K				
52			L				
53			M				
54			N				
55	NOTES:				<p>Sheet Nr. 10</p>	<p>T-104</p>	
56							
57							
58							
59					<p>UNIVERSITAT ROVIRA I VIRGILI Escola Tècnica Superior d'Enginyeria Química Departament d'Enginyeria Química</p>		
	0	Specification T-104	11/05/2012	P. Corbi		P. Corbi	
	REV.	DESCRIPTION	DATE	PREP.		APPR.	

### **4.3. Process description**

The process followed for sunscreen production is a batch process. Therefore, the process is divided into four stages: loading time, mixing time, unloading time and cleaning time.

Basically, the process includes the following steps: fill the batch vessel with warm De-water, add water soluble ingredients and surfactants, this phase is considered to be the aqueous phase. Then, the other compounds are added leading to the oil phase, while it is cooling in the vessel under gentle agitation. The compounds are added following a recipe. A more detailed explanation is found below.

#### **4.3.1. Raw material storage**

##### **4.3.1.1. Solid storage**

Solid raw materials are stored using sacks in the warehouse. The warehouse is at room temperature and atmospheric pressure. It has proper ventilation according to storage conditions determined by the Material Safety Data Sheets (MSDS). Table 4.7 shows the quantities of each material related to their storage and quantities required for the process.

Table 4.7. Characteristics of solid storage.

Compound	Sack amount (kg)	Kg/batch	Number sacks/batch
Laponite XLG	2	8	4
Gelwhite L	10	20	2
Optigel WX	1	1	1
Titanium Dioxide	50	100	2
Dowicil 200	5	5	1

The warehouse is located close to the agitation tank AT-201. To transport these materials the operator uses a wheelbarrow. The compounds are lifted to the level of the walkaround, located on the top of the vessel using an automatic pulley. The compounds are added using a feed hopper (H-201), situated on the top of the same vessel. Obviously, compounds are added following the product recipe.



Figure 4.4. Representation of the structure in agitation tank.

#### 4.3.1.2. Liquid storage

Liquid materials are stored in tanks or bottled. Both according to storage conditions determined in the data sheet of each compound.

Bottles are stored in the warehouse. As already mentioned, they are stored according to the Material Safety Data Sheet (MSDS). Table 4.8 shows the quantities of each compound relating to their storage and quantities required for the process.

Table 4.8. Characteristics of liquid bottles storage

Compound	Bottle size (kg)	Kg/batch	Number bottle/batch
Citric acid	2	2	1
Glycerine	5	5	1

The plant has two storage tanks which are shown in table 4.9. The characteristics of these tanks and storage conditions are in their specification sheets.

Table 4.9. Storage tanks.

Compound	Tank
Dow Corning 200 350 cst	T-102
Pure Thix HH	T-103

### 4.3.2. Formulating the sunscreen

This process is divided in 4 phases. Ingredients are purchased from outside sources and mixed with the deionised water in the agitation tank AT-201. The ingredients are not added at the same time; they are added according to the recipe of the final formulation as it shows in table 4.10.

First, the plant has a stream which supplies De-water from De-water net. Deionised water is purified using a method called reverse osmosis. Reverse osmosis extracts pure, fresh water by forcing water under pressure through a semipermeable membrane which separates the water from salts and other impurities, obtaining much purer water.

Table 4.10. Recipe for sunscreen.

Phase	Ingredient/ INCI	% Weight	Trade Name
<b>A</b>	Water	60.8	Deionesed water
	Sodium Magnesium Silicate	0.8	Laponite XLG
	Bentonite	2.0	Gelwhite L
	Bentonite and Xanthan Gum	0.2	Optigel WX
<b>B</b>	Citric Acid	0.2	Citric Acid
	<b>C</b>	Dow Corning 200 350 cst	20.0
<b>C</b>	GranLux TEMS 45T	10.0	Titanium dioxide
	Glycerine	0.5	Glycerine
<b>D</b>	Preservative	0.5	Dowicil 200
	1,3 Butylene Glycol, water, Polyether-1	5.0	Pure Thix HH

**Phase A:** Fill the vessel with pre-heated deionised water (DE-Water). Water is pre-heated to 60 °C before reaching the agitation tank by a serpentine coil (T-101). Then, add Phase A whilst low-shear energy (500 rpm) is used for phase A for 30 minutes to homogenize until uniform.

**Phase B:** Add Phase B into Phase A while homogenizing and increase the shear energy to homogenize for 15 minutes (700 rpm). Begin cooling to temperature room (17 °C).

**Phase C:** Add Phase C very slowly in small increments, making sure oil is mixed well between additions. Continue mixing at the same higher shear (700 rpm) energy for 30 minutes.

**Phase D:** add Phase D and mix until uniform. It takes 15 minutes.

The whole process lasts 5.34 hours as shown in figure 4.5. The standard cooling time is around 60% of the residence time (ref. 12). In this case the residence time is 185 min per batch, and the cooling time is 110 min.

This plant works 8,000 h/year. The 760 hours left are dedicated to maintenance, to clean the pipes when needed, to change the product to produce in the batch, unexpected situations, shutdown for cleaning the whole plant, etc. Table 4.11 shows the production of the whole time and the process time of each product.

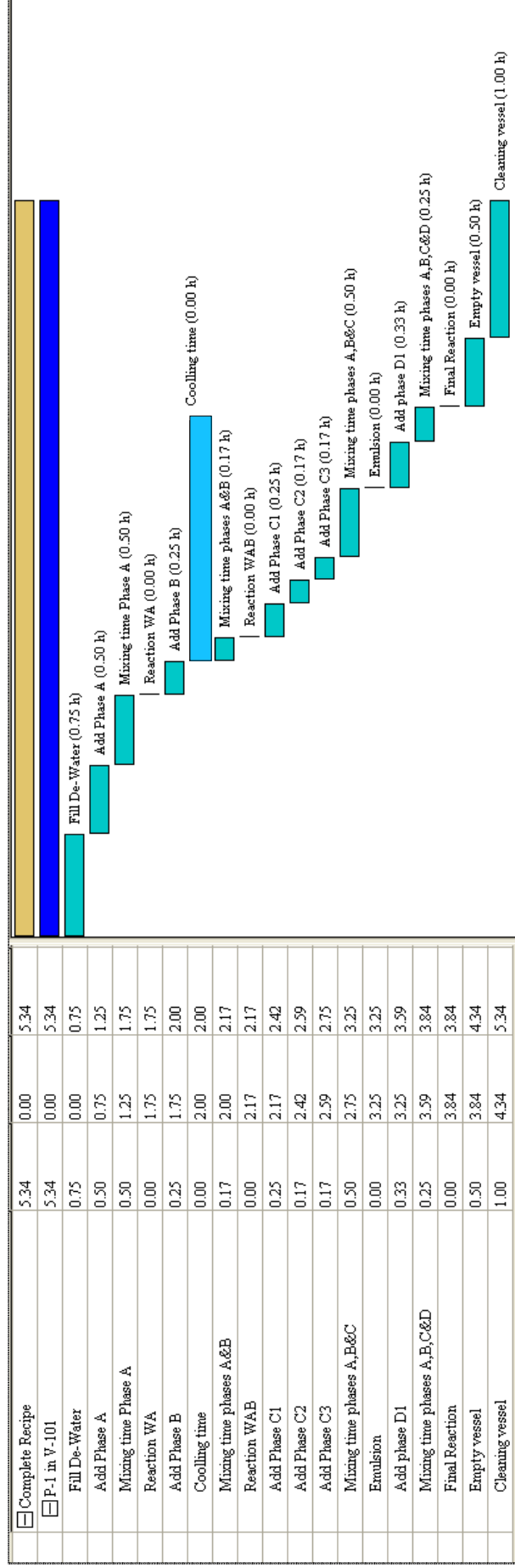
Table 4.11. Characteristics of the process.

<b>Product</b>	<b>Process time (h)</b>	<b>kg/ Batch</b>	<b>N batch/ year</b>	<b>T/year</b>	<b>Hours/year</b>
Sunscreen	5.34	1,000	500	500	2,667
B	5.34	1,000	500	500	2,667
C	5.34	1,000	500	500	2,667
Total			1,500	1,500	8,000

When the product is finish is sent to the storage tank T-104, where the sunscreen is kept at room temperature and atmospheric pressure. The design of the equipments is in chapter 4 section 2 in this report and in appendix 3.

The packaging process and the control quality for the sunscreen are not taken into account of the battery limits.

Figure 4.5. Shows steps and time for 1 batch.



### 4.3.3. Description of emulsion process

This emulsion is an oil-in-water emulsion. To understand the emulsion process, the raw materials are divided in two groups: aqueous phase and oil phase. The aqueous phase corresponds to phases A and B, and the oil phase corresponds to phases C and D (one can see in table 4.12).

Table 4.12. Recipe for sunscreen.

Phase in Emulsion	Raw Material	Recipe phase
Aqueous phase	Deionised water Laponite XLG Gelwhite L Optigel WX	A
	Citric Acid	B
Oil Phase	Dow Corning Titanium dioxide Glycerine	C
	Dowicil 200 Pure Thix HH	D

Figure 4.6 shows the simplified process for emulsion. As follows, the emulsion process is explained briefly according to the recipe and the importance of every raw material.

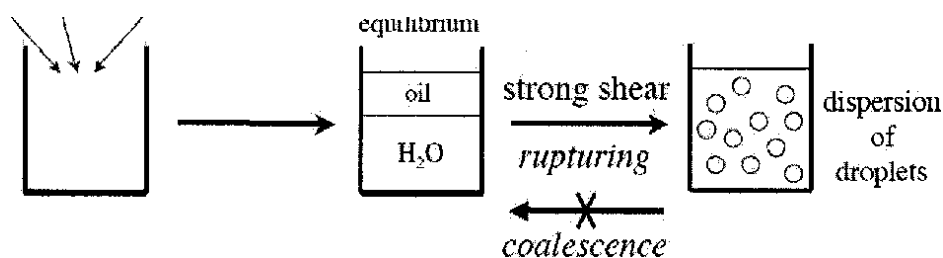


Figure4.6. Simplified emulsion process.

#### 4.3.3.1. Aqueous phase

Aqueous phase is based mainly on water. In this case, the aqueous phase is based on De-Water, stabilizers in powder form (Optigel WX, Gelwhite L and Laponite XLG) and citric acid. The stabilizers (phase A) are hydrophilic and easily dispersed in water. However, the use of warm water facilitates and accelerates the dissolution into water. The use of shear dispersion equipment ensures complete dispersion and offers maximum efficiency. The

compounds should be introduced into the water at the initial dispersion phase prior to adding other ingredients. Optimal efficiency depends on complete hydration and ultimate dispersion of the stabilizers. Therefore, stirring under high shearing forces for 20 - 45 minutes is recommended.

Optigel WX is a specially selected and activated smectite product that has a high swelling capacity in water and shows a marked thixotropic thickening effect. It is stable in diluted acids and bases and is particularly effective in acidic media. Gelwhite L is a highly purified montmorillonite refined from selectively mined natural white bentonite deposits.

The high ion exchange capacity of these materials is ideal for adsorption of oils. Gelwhite L is ideal for creams and topical which requires body, texture, thixotropy, suspension and stability. Laponite XLG is a synthetic layered silicate with low heavy metals content.

Laponite is used in products to control viscosity and flow properties in water based solutions. In chapter 5, the properties of laponite are more thoroughly explained.

After the mixing time that it is required, a small amount of citric acid (phase B) is added. This material is important for two reasons: increases the pH to improve the emulsion process, and is a preservative to help to avoid the development of microorganisms.

#### **4.3.3.2. Oil phase**

Once the stabilizers and the acid citric are added (phases A&B), the cooling process starts and the oil phase is added. At the same time, the shear of agitation is increased. First, Dow Corning, titanium dioxide and glycerine (phase C) are added. Dow Corning is a medium viscosity polymer which is used to increase the viscosity of the emulsion. Titanium dioxide is a physical sunscreen protecting agent against UVB and short UVA light. It has a long history of seemingly safe use and is not irritating. Glycerine is a colourless, odourless, viscous liquid. Glycerine easily dissolves in water. It improves smoothness of the skin and moisture content. It is a compound that keeps the skin moisture while providing a cooling effect.

None of them can be dissolved in water, not even partially, but in this case, through mixing and the use of stabilizers makes it possible. Finally, Dowicil 200 and Pure Thix HH are added

(phase D). Dowicil 200 is a preservative for antimicrobial protection in cosmetic and personal care formulations. Pure Thix HH is a clear aqueous solution designed especially for thickening of personal care formulations.

All these compounds work together to create a product that appeals to the aesthetic perceptions of the consumer.

#### **4.3.4. Installation description**

Details of location are described in section 3.2.3 and more specifically in Figure 3.1. This chosen plot is rectangular with an area of 0.07 km<sup>2</sup> (362 m x 203 m) and it is inside a building. The area occupied by the new plant is designed according to the regulations in South of Australia and MIE AQP1.

Following chapters show specific coordinates for the equipment in this plant. The source axes (X, Y) are located at the centre of the most important equipment, the agitation tank AT-201. The distance is measured from the centre of the Agitation tank AT-201 to the centre of each equipment in the plant.

The plant was divided into three zones, previously explained in section 4.1.4.; zone of raw compounds, mixing zone, and zone of final product.

Obviously, the mixer zone is not taken into account, as the only equipment found there is the Agitation tank-201.

##### **4.3.4.1. Zone of raw compounds**

This zone is 261 m<sup>2</sup> (58 m x 4.5 m) and it contains storage tanks T-102 and T-103 along with a tank to heat the deionised water T-101 from water net. Spills containers have a slope of 1%.

Table 4.13. Description of zone raw material.

<b>Name</b>	<b>T-101</b>	<b>T-102</b>	<b>T-103</b>
<b>Inlet</b>	P101-1"-SA	-	-
<b>Outlet</b>	P102-3/8"-SA	P201-1/4-SA	P301-3/8"-SA
<b>X (m)</b>	-11.0	-9.5	-9.8
<b>Y (m)</b>	5.0	0	-3.5

<b>Position</b>	Vertical	Vertical	Vertical
<b>Facility closer NS/SN</b>	-- /T-102	T-101/T-103	T-102/ --
<b>Distance NS/SN from facility closer</b>	-- /-5.0 m	5.0 m/-3.05 m	3.05 m/ --
<b>Facility closer EW/WE</b>	-- /P-101A	-- /P-102A	-- /P-103A
<b>Distance EW/WE from facility closer</b>	-- /5.5 m	-- /4 m	-- /4 m

#### 4.3.4.2. Final product zone

Even if this zone has several tanks to store the products that this plant produces, in battery limit it is only has into account the tank for final product (T-104). This zone is 135 m<sup>2</sup> (7.5 m x18 m).

Table 4.14. Description of the mixing zone.

<b>Name</b>	<b>T-104</b>
<b>Input</b>	P402-1/2''-SA
<b>Output</b>	-
<b>X (m)</b>	21.0
<b>Y (m)</b>	0
<b>Position</b>	Vertical
<b>Facility closer NS/SN</b>	---
<b>Distance NS/SN from facility closer</b>	----
<b>Facility closer EW/WE</b>	P-104A /P-501A
<b>Distance EW/WE from facility closer</b>	6.5/ -15.0 m

## **5. RHEOLOGICAL STUDY OF LAPONITE**

The effectiveness of any sunscreen product is critically dependent on the formation of an even, continuous product film on the skin, and a homogeneous distribution of physical sunscreen within that film. Therefore, the rheological behaviour of the formulation has a large effect on the SPF (Sun Protection Factor). For more details about SPF see appendix 6.

In order to fully understand the factors influencing efficacy of sunscreen, it is necessary to consider what actually happens when the emulsion is applied on the skin.

For that reason, it is decided to study one of the clay particles used as stabilizer on this sunscreen laponite. It is important to mention that the laponite used in the experiments is Laponite RD and the one used to elaborate sunscreen is laponite XLG. However, the properties are quite similar, but laponite XLG is more common in personal care products due to its higher purity.

An article called “Laponite-stabilised oil-in-water emulsions viscoelasticity and Thixotropy” was published as the result of this study. The article can be found in appendix 4.

### **5.1. Introduction**

Emulsions are dispersions of droplets of one fluid mixed into an immiscible continuous phase of another fluid. The addition of surfactant is necessary to provide a short-range repulsion between the oil-water interfaces which inhibits droplet coalescence and can stabilize the emulsion (ref. 13).

In addition to using conventional surfactants or surface-active polymers as both the emulsifier and stabiliser for macroemulsions of oil and water, colloidal solid particles are also effective. Although many commercial emulsion formulations contain combinations of surfactants/polymers and solids, e.g. cosmetic preparations, it is possible to prepare stable emulsions using solid particles alone. Emulsions of this kind are often referred to as Pickering emulsions after his early work on such systems (ref. 14).

It was demonstrated that for systems stabilised by particles of intermediate hydrophobicity, emulsion type varied with the type of oil (polar or non-polar) and the composition of the

aqueous phase (ref. 15). Very few studies exist however in which clay particles have been used as stabilisers in preparing emulsions (ref.17-20).

Viscosity can be determined by applying a shear rate to a sample and measuring the viscosity and stress data obtained. The viscosity of most colloidal suspensions, at steady state, follows pseudo-plastic behaviour with power law dependence on shear rate, even at very low shear rates. After remaining at rest for a long time, the system shows the maximum viscosity or zero shear rate viscosity (ref.21)

Studying the mechanical behaviour of these materials is complicated for the fact that their response is viscoelastic, intermediate between that of solids and liquids. Oscillatory rheology is a standard experimental tool for studying such behaviour; it provides new insights about the physical mechanisms that govern the unique mechanical of this materials.

The oscillatory of o/w of monodisperse emulsions was investigated by *A. Weitz*. He resolved that emulsions exhibit a plastic-like response to shear deformations; for small deformations, they resist the shear elasticity, with the stress,  $\tau$ , being linearly proportional to the strain,  $\gamma$ . However, for large enough deformations, they flow, offering comparatively much less additional resistance. A statistic calculation of dependence of the stress on the strain at fixed  $\omega$  shows a linear dependency at small strains,  $\tau = G' \gamma$ , where  $G'$  is the elastic modulus and finally, at high strain, stress drops abruptly. For oscillatory measurements, he obtained at lower stress is linear in the strain,  $\tau \sim \gamma \text{ Tan } \delta (G''/G')$  where  $G''$  is loss modulus, is independent of strain, and  $G'$  and  $G''$  are independent of  $\gamma$  at lower strain and constant frequency,  $\omega$  (ref. 17).

Thixotropic behaviour is commonly encountered in emulsions used in creams, sauces, inks and drilling muds. Thixotropy can be defined as the tendency of matter to exhibit a time-dependent change in its reference properties (reference viscosity, yield value, time scale, elasticity modulus, loss modulus, etc. A thixotropic fluid is a fluid which takes a finite time to attain equilibrium viscosity when is introduced a step change in the shear rate.

Recently it was shown the thixotropic response of surfactant-stabilised emulsions can be controlled by loading time the emulsions with clay particles (ref. 22).

Understanding the mechanisms that cause this complex rheological behaviour is of vital importance when using materials and in controlling the industrial processes in which they are involved (ref. 23).

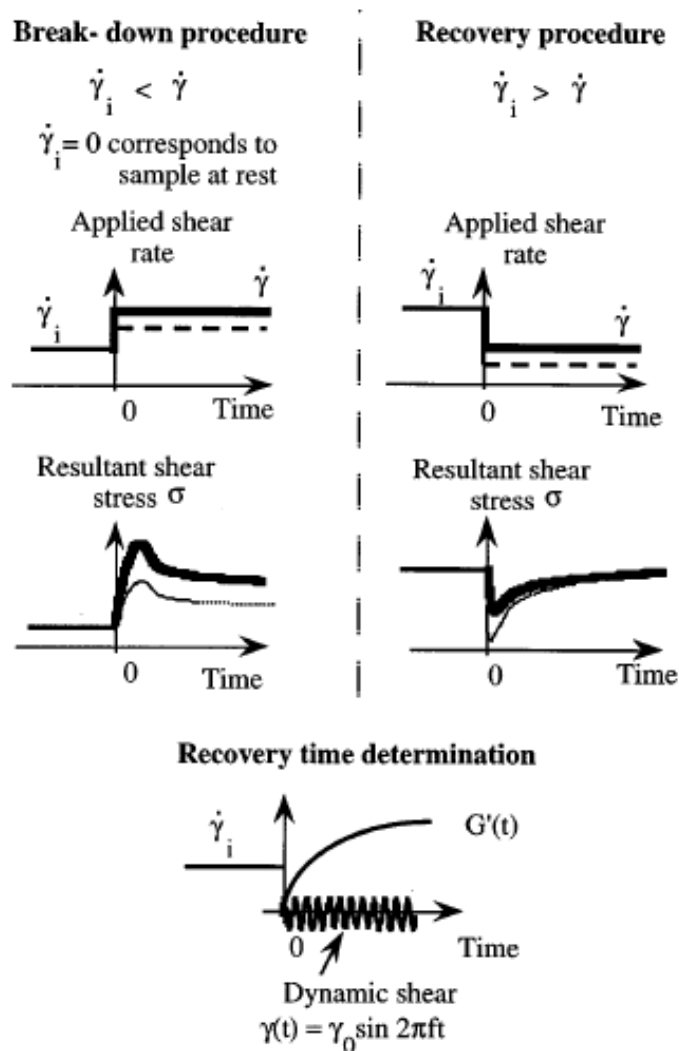


Figure 5.1. Procedures for characterizing thixotropic behaviour.

The breakdown and recovery behaviour of the dispersion are measured to help understand the thixotropic mechanism. When shear is applied, structures break down and the material starting from a sufficiently long rest state, the viscosity decreases with time. Once the shear applied ceases, the material gradually recovers consistency and the structure that it had at rest, as it shown in figure 5.1 (ref. 23).

It has been decided to study the properties of emulsions stabilised by synthetic clay, Laponite RD ( $\text{Si}_8\text{Mg}_{5.45}\text{Li}_{0.4}\text{H}_4\text{O}_{24}\text{Na}_{0.7}$ ) of high purity with small and uniform particle size. Laponite

forms discrete clear dispersions in water containing discrete particles, similar to circular discs of diameter ca. 30 nm and thickness ca. 1 nm. The effects of clay particle concentration and salt concentration, stability and average drop size of bromohexadecane-water emulsions are determined and discussed in relation to the dispersions.

Aqueous laponite dispersions show different physical states (viscoelastic gel, elastic solid, etc) depending on laponite concentration and salt concentration. The phase diagram (ref. 24) of alkaline dispersions is in figure 1. At high pH, electrical charges result in mutual repulsion at low levels of salt concentration. This forms a gel-like material at high particle concentration and pseudoplastics fluid at low particle concentration of laponite. As the salt concentration is increased the systems begins to flocculate leading to a weaker yield stress.

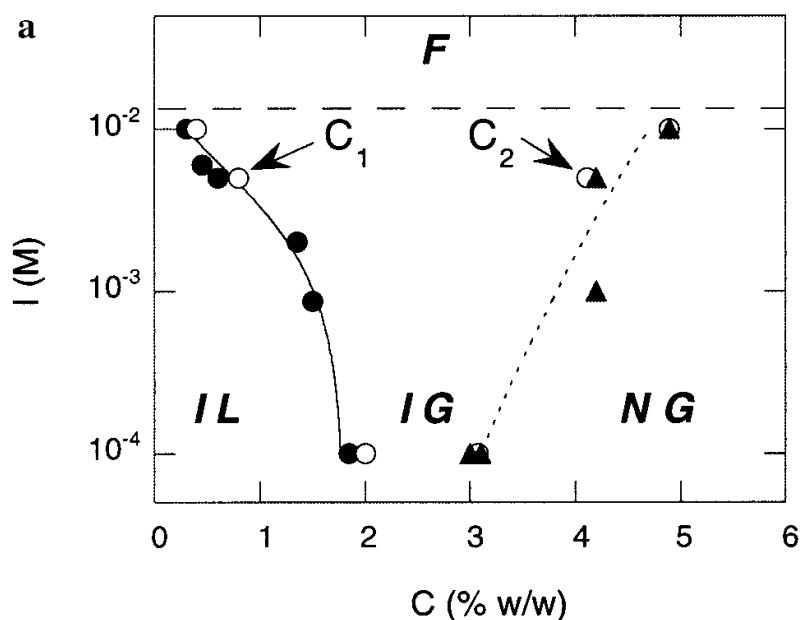


Figure 5.2. Phase diagram for laponite dispersions as obtained from (●) rheological, (○) osmometric and (▲) birefringence data: *F*, floc; *IL*, isotropic liquid; *IG*, isotropic gel; *NG*, nematic gel.  $C_1$  and  $C_2$  are the limits of the plateau where the suspensions are isotropic gels.

Therefore, the dependence of the viscosity, oscillatory and rheology has been studied for different volume oil fractions ( $\phi$ ), salt and laponite concentrations, as well as, the thixotropic behaviour of dispersion and emulsion at low volume fractions.

For viscosity and oscillatory measurements, a viscosity test and strain sweep test and frequency sweep test, have been used respectively. For measuring the thixotropic behaviour the breakdown and recovery tests have been applied.

## 5.2. Experimental

### 5.2.1. Materials

- Water: was obtained by a Milli-Q reagent water system, which reduces the conductivity to 2.6 MΩ-cm.
- Sodium Chloride (NaCl): was provided as white powder by Chem-Supply Industries Ltd. It has a purity of 99.0 wt%.
- Oil: bromohexadecane. This oil has a purity >99%. It was columned at least twice through aluminium oxide in order to remove polar impurities.
- Others oils: Isopropyl Myristate and dodecane. These oils, all have a purity >99%. Isopropyl Myristate was columned at least twice through aluminium oxide in order to remove polar impurities.
- Laponite RD: was provided as a white free-flowing powder by Rockwood Industries Ltd.
- Rhodamine B: was provided by BDH Chemicals Industries Ltd.

### 5.2.2. Instruments

- Ultra Turrax homogeniser X1030D: is an intensive blender of different insoluble phases, (rotor-stator) with 1,5 cm head.
- Beakers: material glass and volume 25 ml. (diameter 3 cm, height 5 cm), provided by Hysis.
- Rheometric rheometer: is a controlled stress/controlled strain rheometer at a temperature of  $25 \pm 0.1$  °C. It is also capable of performing dynamic measurements. The instrument is capable of working with a number of different geometries. Table 5.1, shows the characteristics of the geometries used. The software used was RSI Orchestrator which is capable of exporting the data to an Excel file and to interpret the results from the rheology test.

Table 5.1. Characteristics of the geometries.

Sensor	Temperature Control	Shaft	Temperature sensor
40 mm cone	Peltier	Short	Peltier
25 mm cone	Peltier	Short	Peltier

- Confocal fluorescence microscopy (CFM, Leica SP5 spectra scanning confocal microscope): was used to visualise dispersions and emulsions prepared containing Rhodamine B (Sigma, 97%). At the low concentration used ( $\sim 0.3$  M) the dye adsorbs completely onto the laponite particles. The samples were excited at a wavelength of 514 nm and the fluorescence emission intensity collected over 555 to 655 nm.



Figure 5.3. Rheometric Rheometer.

### 5.2.3. Methods

#### 5.2.3.1. Preparation of laponite RD dispersions in aqueous solution

1. Weight out appropriate amounts of laponite powder using an analytical balance. Add known amount of aqueous NaCl concentration into the beakers. Fixed pH values of 9 were used.
2. Mix the dispersions using the Ultra Turrax homogeniser X1030D operating at setting 1 ( $11,000 \text{ min}^{-1}$ ) for 2 minutes to ensure the dispersion is uniform.
3. Pour the dispersions into sample vials: Keep in bath for 24 hours at 25 °C.

### **5.2.3.2 Preparation Laponite RD of emulsions in aqueous solution**

1. Follow the steps 1, 2 and 3 of Preparation of laponite RD dispersions in aqueous solution.
2. Add 1 ml of the different oils ( $\phi=0.10$ ) to each dispersion. Homogenise each liquid mixture using Ultra Turrax homogeniser X1030D at setting 2 (13,000 min<sup>-1</sup>) for 1 minute.
3. Pour the dispersions into sample vials. Keep in the bath for 24 hours at 25 °C.

### **5.2.3.3. Preparation of emulsions and dispersions to analyze in optic microscope**

1. Dissolve 0.0005 g of Rhodamine B in 100 ml of MilliQ water in a large screw cap jar. Cover jar with al foil to protect the fluorescent solution from light. Wear gloves when handling the solid and the solutions.
2. Add 2 drops of Rhodamine B solution to the dispersion of emulsion before mixing.
3. Place samples tubes inside the plastic jar with lid (to protect fluorescent emulsions and dispersions from light) and place the jar in the water bath until they are analyzed.

## **5.2.4. Rheology**

Rheology experiments were done using a Rheometrics rheometer and RSI Orchestrator as a software. Two different geometries were used depending on the test and behaviour flow of the sample and the test. There was a fixed gap of 0.05 mm for both geometries. All the tests were kept at a constant temperature of  $25 \pm 0.5^\circ\text{C}$ . The rheology experiments were divided into 2 different experiments.

### **5.2.4.1. Viscosity test**

Viscosity test: obtains the viscosity variation in function of shear rate of the suspensions and emulsions. Measurements were made using cone plate geometries. The samples were placed between the plate cone geometry (40 mm or 25 mm) and a plate. The shear rate was increased from 1.0-1000 s<sup>-1</sup>.

#### 5.2.4.2. Oscillatory

The oscillatory measurements are made by sweeping the strain from 0.239 to 100% at a fixed frequency between 10-30 Hz. Frequencies determine the yield stress and yield strain, but it also causes the emulsion to yield along the flow direction. The oscillatory measurement is the best for determining the yield strain because the departure from the linear regime of rheology is controlled (ref. 13).

Strain sweep test: the material response to increasing deformation from strain, it is monitored at a constant frequency. It is used to identify Linear Viscoelastic Region (LVR).

This test obtains the storage modulus ( $G'$ ), loss modulus ( $G''$ ),  $\tan \delta$  (tangent between  $G''$  and  $G'$ ) and stress ( $\tau$ ) variations in function of strain ( $\gamma$ ) in (%) of the suspensions and emulsions in the range of 1.0-100 (%). The samples were placed between the plate cone geometry (40 mm or 25 mm) and a plate. The sample placed was subjected to weak sinusoidal excitation and the viscoelastic modulus was recorded versus strain (%).

To do the test, a value of frequency between 10-30 Hz was chosen. At high viscosity behaviour the chosen frequency was 10 Hz, whereas, at low viscosity behaviour 30 Hz was chosen, yielding better results.

Frequency sweep test: the material response to increasing frequency, it is monitored at a constant strain. It is used to identify the elasticity (reversible deformation in materials).

This test obtains storage ( $G'$ ), and ( $G''$ ) loss modulus,  $\tan \delta$  (tangent between  $G'$  and  $G''$ ) and stress ( $\tau$ ) variations in function of frequency ( $\omega$ ) (%) of the suspensions and emulsions in the range of 1.0-100 (rad/s). The samples were placed between the plate cone geometry (40 mm or 25 mm) and a plate. The sample placed was subjected to weak sinusoidal excitation and the viscoelastic modulus was recorded versus strain (%).

To do the test, the strain located in the middle of the viscoelastic region was chosen. Therefore, the average of  $G'$  was obtained.

Breakdown test: stress response of viscoelastic material in applying shear rate during a defined time. It is used to identify the structural changes.

This test obtains the stress,  $\tau$ , in function of time (sec) of suspensions and emulsions fixing the preshear ( $s^{-1}$ ). The samples were placed between a plate with a cone geometry (25 mm) and a plate.

Recovery test: is performed by applying shear rate to the material. When the stress is removed the material is allowed to recover. It is used to study the structural changes and to study materials under low shear rates or frequencies, under long test times.

This test obtains the storage modulus,  $G'$ , in function of time (sec) of suspensions and emulsions fixing the steady preshear ( $s^{-1}$ ), preshear rate ( $s^{-1}$ ), preshear time ( $s^{-1}$ ), and delay before test (sec). The samples were placed between a plate with cone geometry (25 mm) and a plate.

## 5.2.5. Results and discussion

### 5.2.5.1. Dispersions of laponite RD in aqueous solution

Laponite RD was successfully dispersed in NaCl solutions at concentrations ranging from 0.002 to 0.01 M. As follows it shows the flow and behaviour study of 3 dispersions. This study was performed over 5 days.

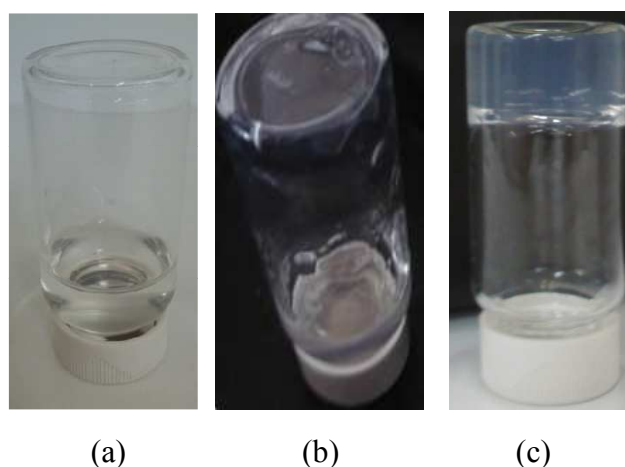


Figure 5.4. Inverted sample tubes of laponite dispersions at 0.01 M of NaCl 24 h after preparation. (a) 0.5 wt% laponite, (b) 1.5 wt% laponite, (c) 2.0 wt% laponite.

Figure 5.4 shows examples of dispersions prepared in 0.01 M NaCl. All dispersions are clear or slightly turbid. For concentrations down to 0.5 wt% laponite, the dispersion flows, as shown in figure (a). Dispersion remained clear and non-viscous during the 5 days. For concentrations between 1.0-1.5 wt% laponite, dispersion is a clear and viscous gel with low viscosity. It is stuck on the wall of the inverted vial, as shown in figure (b). For concentrations of 2.0 wt% laponite, dispersion remained clear and non-viscous as shown in figure (c). Viscosity of the dispersions appears to increase slightly over 5 days.

#### **5.2.5.2. Emulsions of bromohexadecane, aqueous NaCl and Laponite RD**

Emulsions were prepared from different types of oil and laponite concentration. The aim was to link the behaviour of emulsions to the structure of the aqueous dispersions to choose the proper oil.

Emulsion made from bromohexadecane oil remained stable during the 5 days and it does not show creaming. Emulsions made from isopropyl myristate and dodecane oil show creaming and coalescence giving separated water and oil phases, respectively. Therefore, Bromohexadecane is chosen as oil to prepare stable emulsions from oil-water mixtures containing Laponite RD particles.

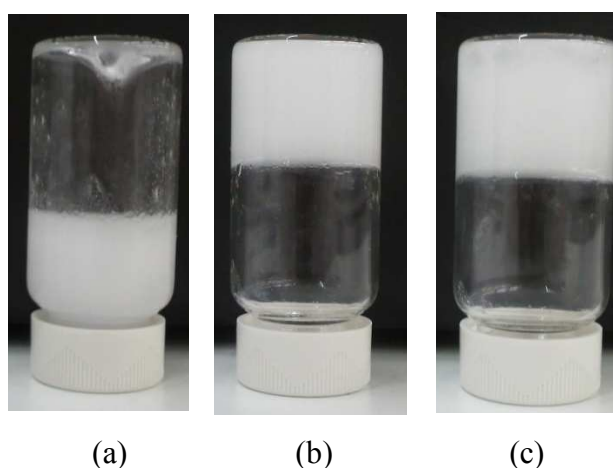
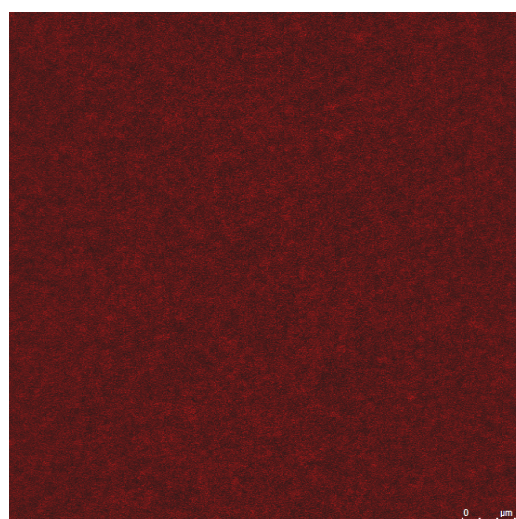


Figure 5.5. Inverted samples tubes of laponite emulsions at 0.01M of NaCl and volume fraction oil=0.1, 24h after preparation. (a) 0.5 wt% laponite, (b) 1.5 wt% laponite, (c) 2.0 wt% laponite.

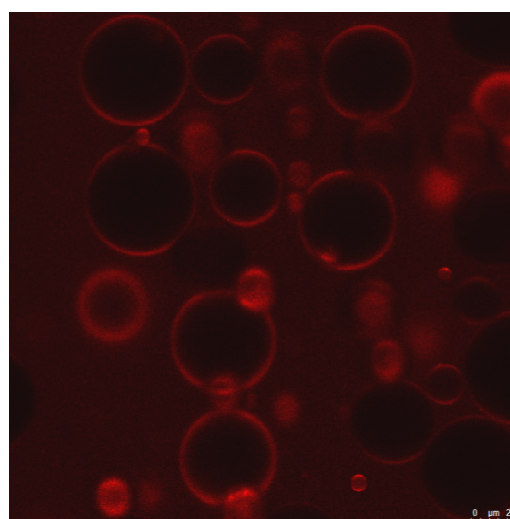
In figure 5.5, one can see the appearance of emulsions after 24 h after preparation. At low laponite concentration (0.5 wt%), emulsion flows, as shown in figure (a). At higher Laponite RD concentration, as shown in figures (b) and (c) emulsions exhibit non-viscous behaviour. Viscosity of the emulsions increases slightly during the 5 days.

### 5.2.5.3. Microscope analysis

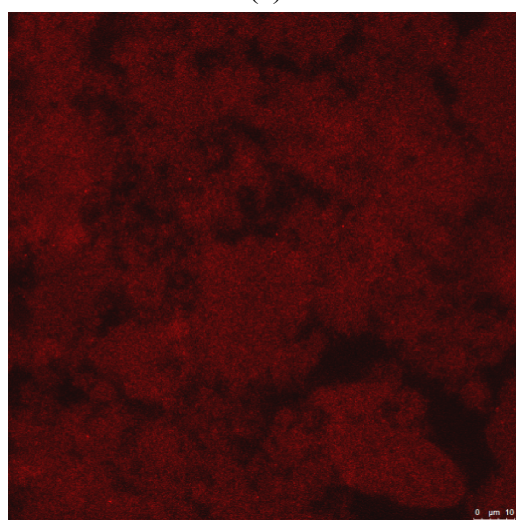
Figure 5.6 shows the optical micrographs of 4 different samples. Rhodamine B was used to obtain the contrast. Figures (a) and (c) are dispersions at different laponite and salt concentration and figures (b) and (d) are the emulsions of the dispersion of (a) and (c), respectively.



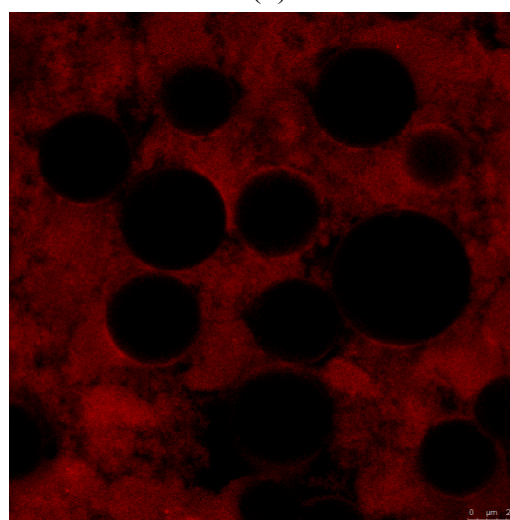
(a)



(b)



(c)



(d)

Figure 5.6. Optical micrographs of dispersions and emulsions. (a) 2.2 wt% laponite, 0.002 M  $\sigma=0$ ; (b) 2.2 wt% laponite, 0.002 M  $\sigma=0.20$  bromohexadecane; (c) 1.0 wt% laponite, 0.01 M  $\sigma=0$ ; (d) 1.0 wt% laponite, 0.01 M  $\sigma=0.20$  bromohexadecane.

Comparing figure (a) and (c), dispersions at different laponite and salt concentration, shows that at low salt concentration, the network is not strongly established, however, at high laponite and salt concentration the network is better established.

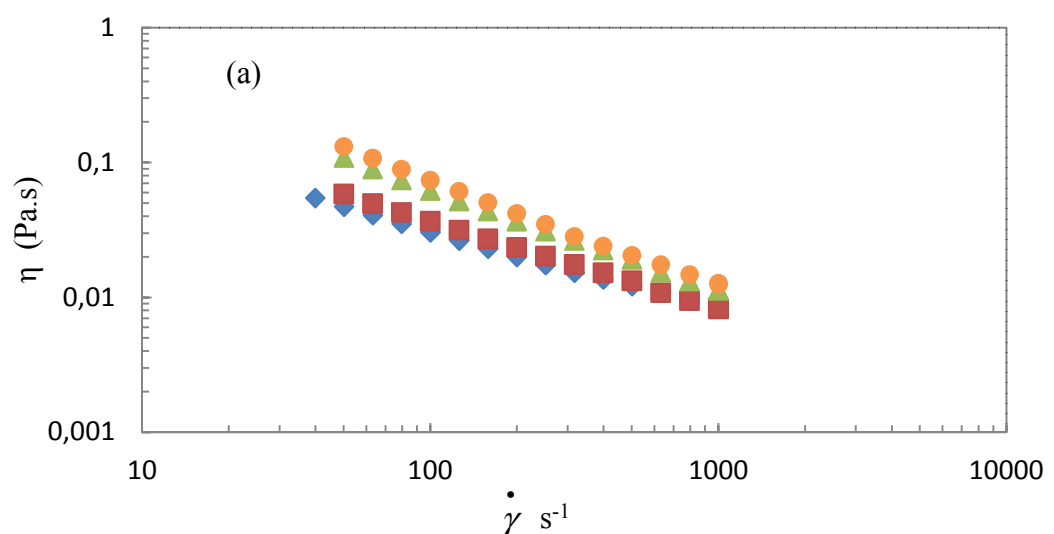
Figures (b) and (d) show emulsions of different laponite and salt concentration. Both show the location of the clay particles at the interface of the drops to produce a barrier that avoids the coalescence of drops.

#### 5.2.5.4. Rheology

As already mentioned, rheology is the science of deformation and flow of matter under controlled testing conditions. The different experiments undertaken are as follows:

##### 5.2.5.4.1. Viscous flow

Experiments were performed to determinate the proper range of viscosity for breakdown test.



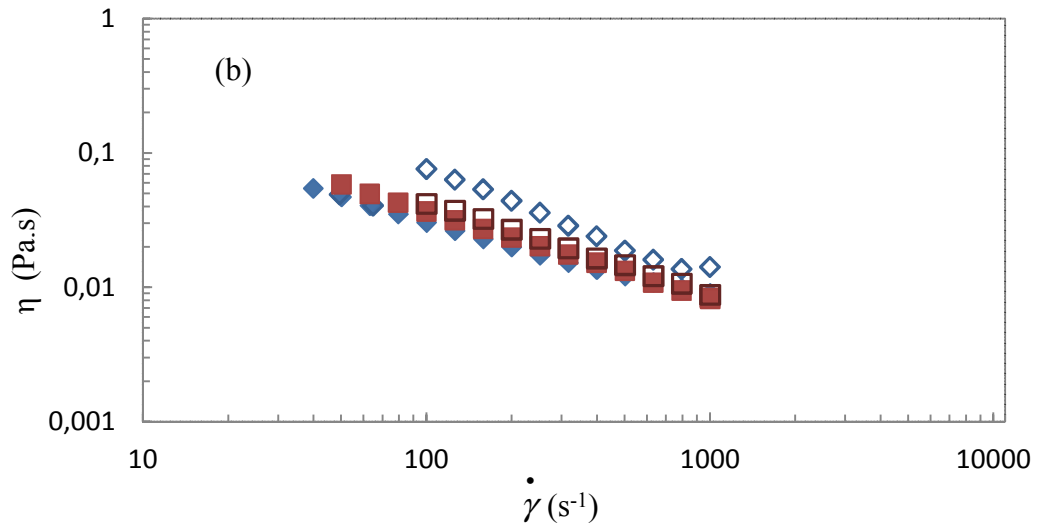


Fig 5.7. a) Variation of the viscosity ( $\eta$ ) as a function of shear rate ( $s^{-1}$ ).

(a) Different concentration of laponite RD: 1.6 wt% ( $\blacklozenge$ ); 1.8 wt% ( $\blacksquare$ ); 2.0 wt% ( $\blacktriangle$ ); 2.2 wt% ( $\bullet$ ); and the same concentration of salt 0.002 M. (b) Comparing the evolution of viscosity for the same sample (1.6 wt % 0.002 M) measured at day 1 ( $\blacklozenge$ ); and at day 8 ( $\blacklozenge$ ) and comparing same laponite concentration (1.8 wt %) at different concentration of salt: 0.002 M ( $\blacksquare$ ) and 0.01 M ( $\square$ ).

Figure 5.7 shows viscosity increases at more laponite RD concentration. Viscosity behaviour decreases as shear rate increases as it shown in figure 5.7.a and 5.7.b, as expected. Viscosity behaviour increases in time as shown in figure 5.7.b, when compared to results of the same sample one week later. Viscosity increases in high concentration salt as shown in figure 5.8, when compared to two different salt concentrations.

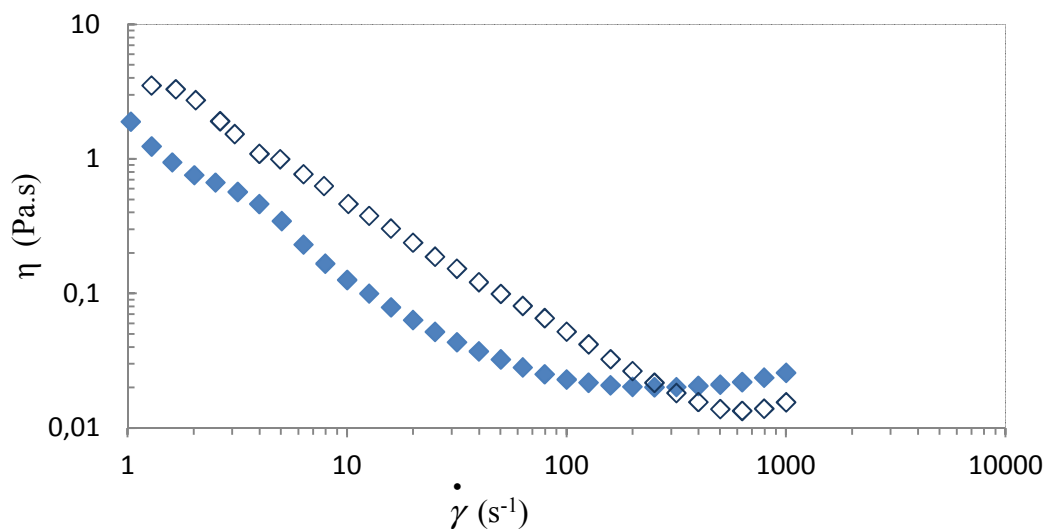


Figure 5.8. Variation of the viscosity ( $\eta$ ) as a function of shear rate ( $s^{-1}$ ) for an emulsion ( $\phi=0.10$ ) ( $\diamond$ ); and dispersion ( $\phi=0$ ) ( $\blacklozenge$ ); at same concentration of laponite RD (1.0 wt% laponite) and 0.01 M NaCl.

Figure 5.8 shows viscosity behaviour of emulsion is higher than the viscosity of dispersions at the same concentration of salt and laponite RD. At a fixed drop size, viscosity increases with oil volume fraction.

#### 5.2.5.5. Oscillatory

Viscoelastic properties of laponite dispersion as a function of laponite RD concentration were obtained by oscillatory measurements.

##### 5.2.5.5.1. Strain sweep test

The aim of the strain sweep test is to identify the Linear Viscoelastic Region (LVR). This allows the proper application of stress during the frequency sweep test.

For the oscillatory measurement, a sinusoidal strain, of peak amplitude,  $\gamma$ , is applied at a frequency,  $\omega$ , and the sinusoidal stress,  $\tau$ , response is measured.

Figures 5.9.a and 5.9.b show the strain dependence of stress and  $\tan \delta$ , respectively. Figure 5.9.a (stress) shows that for a low strain applied (0.1-10 %), the stress increases as a function of strain. Above 10% of strain, the stress remains constant and it does not show dependency on the strain. Figure 5.9.b shows  $\tan \delta$  which is the relation between  $G''$  and  $G'$  ( $\delta=G''/G'$ ).

Figure 5.9.c ( $G'$  and  $G''$ ) shows storage modulus  $G'$  and loss modulus  $G''$  in function of strain,  $\gamma$ . At the smallest  $\gamma$ ,  $G'$  and  $G''$  are dependent on strain, reflecting the linear behaviour. At large strain the emulsion begins to yield and the microstructure of the emulsion is permanently changed.

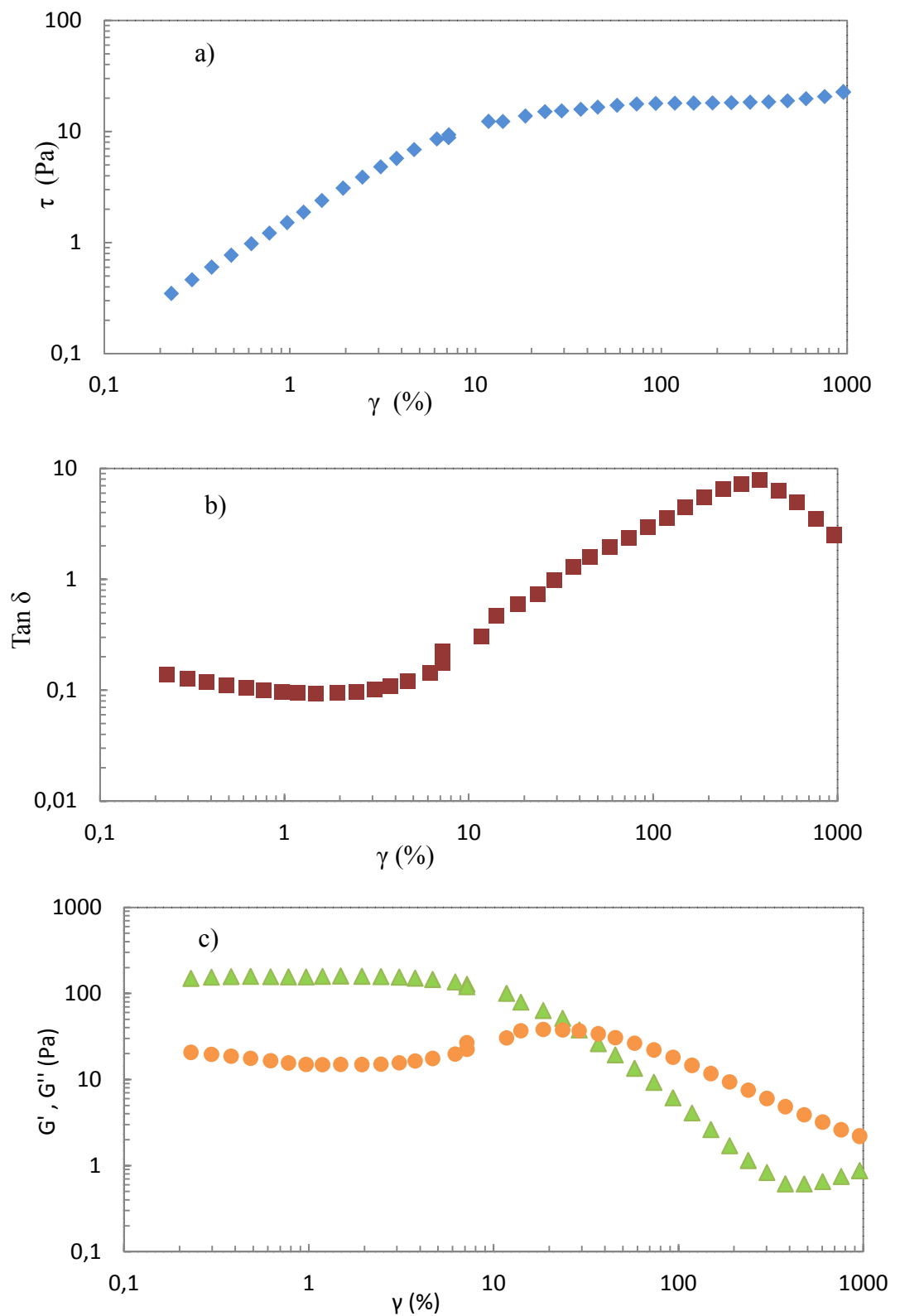


Figure 5.9. Oscillatory shear measurement at 30 Hz of (a) the peak stress,  $\tau$ , (b)  $\tan \delta$ , and (c) stored modulus,  $G'$  (▲) and loss modulus,  $G''$  (●) as a function of peak strain,  $\gamma$ , for a emulsion of 0.002 M, 1.6 wt% laponite, volume fraction ( $\phi=0.40$ ).

When the stress-strain relationship is independent, the linear storage and loss modulus are no longer strictly appropriate to descriptions of the emulsion rheology because they begin to depend strongly on  $\gamma$ .

The power law has several orders of magnitude in  $\gamma$ , it can conveniently define yield strain  $\gamma_v$  and yield stress,  $\tau_v$ , by the intersection of the extrapolations of the low strain linear power law and the high strain sublinear power law. This intersection indicates the limits of viscoelastic and elastic region.

#### 5.2.5.5.2. Frequency sweep test

The frequency,  $\omega$ , dependence of the modulus  $G'$  was measured in the Linear viscoelastic region (LVR).

Figure 5.10 shows the evolution of  $G'$  and  $G''$  in function of the frequency at constant strain. It is observed that  $G'$  remains stable during frequency increases. The average  $G'$  value was used to characterise the dispersion and emulsion viscoelasticity.

To obtain the proper value for the strain, the medium value of the viscoelastic region was chosen in stress line. Figure 5.10 corresponds to a 1 Pa of strain.

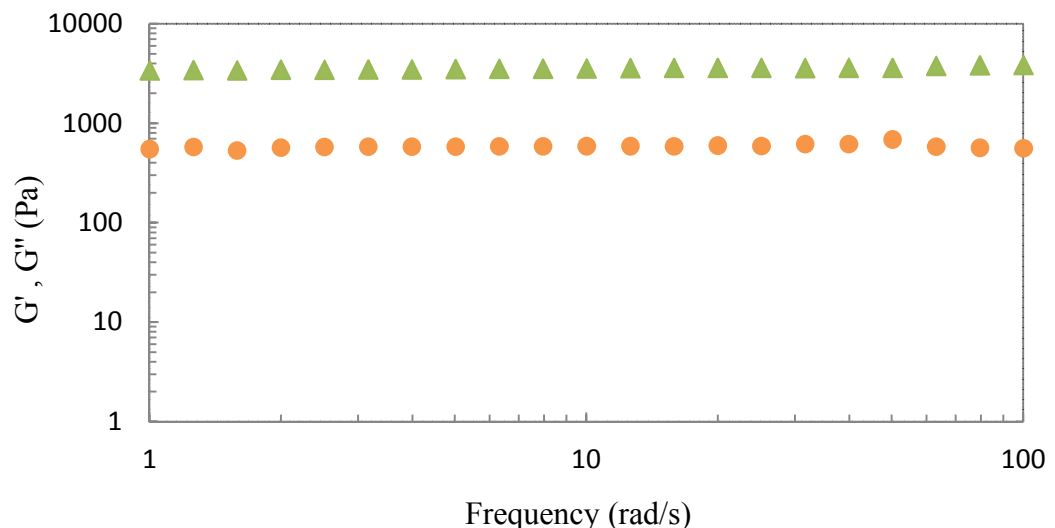


Figure 5.10. Oscillatory frequency measurement at  $\gamma = 1$  Pa of the viscoelastic,  $G'$  ( $\blacktriangle$ ) and elastic modulus,  $G''$  ( $\bullet$ ) for a laponite emulsion for an emulsion of 0.002 M, 1.6 wt% laponite, volume fraction ( $\phi = 0.40$ ).

**5.2.5.5.3. Dependence of laponite particle concentration**

There is a certain particle concentration below which the suspensions do not have a yield stress; and where  $G'$  is lower than  $G''$ . This observation is shown in figure 5.11 and it is the first important observation. As already mentioned,  $G'$  increases with higher particle concentration. According to this interesting evolution,  $G'$  can be written as is shown in equation 5.1 at fixed salt concentration.

$$G' = A(C_{lap} - C_{lap}^*)^\alpha \tag{5.1}$$

Where  $C_{lap}^*$  is a good estimation for the solid fraction above which a viscoelastic gels appears.  $C_{lap}^*$  is a parameter which depends on the salt concentration and the laponite concentration. All  $G'$  data can be plotted versus  $(C_{lap} - C_{lap}^*)$ .

The results obtained in figure 5.11, shows a linear tendency where all the experimental points are set in a master curve given by equation 5.1. The results are that the amplitude  $A$  and the exponent  $\alpha$  ( $=1.98$ ) are independent of laponite and salt concentration. Parameter,  $C_{lap}^*$ , was obtained by phase diagram of laponite dispersions.

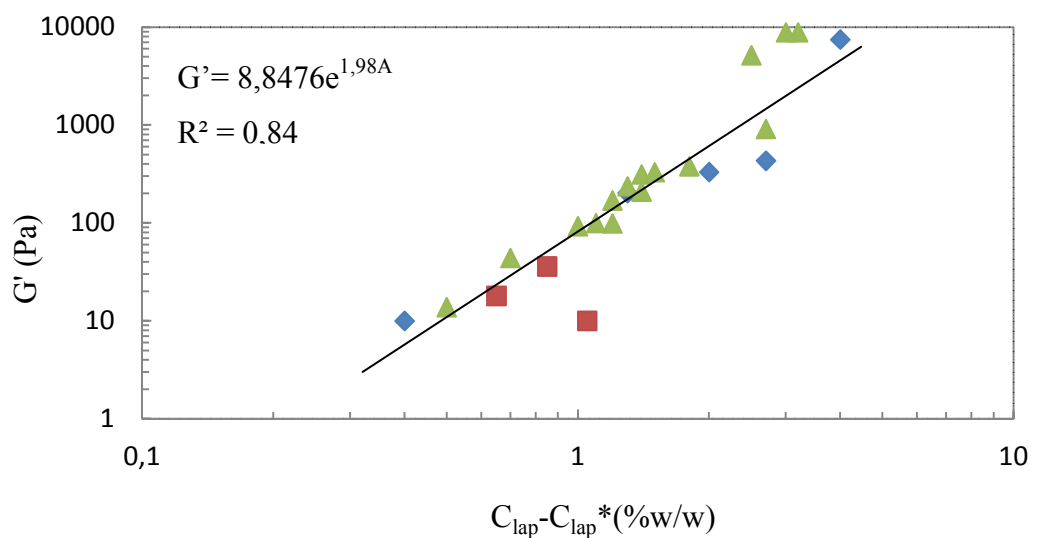


Figure 5.11. Variation in the elastic modulus ( $G'$ ) of laponite dispersions as a function of  $(C_{lap} - C_{lap}^*)$ , for a different salt concentration of 0.002 M (■) and  $C_{lap}^*=1.35$  % w/w; 0.005 (◆) and  $C_{lap}^*=0.6$ % w/w and 0.01 M (▲) and  $C_{lap}^*=0$  % w/w.

#### 5.2.5.5.4. Dependence of storage modulus $G'$ of volume fraction

Figure 5.12 shows the dependence between the averages of storage modulus  $G'$  and different oils fraction concentration for the same sample. As already mentioned, the averages of  $G'$  were obtained by frequency sweep test.

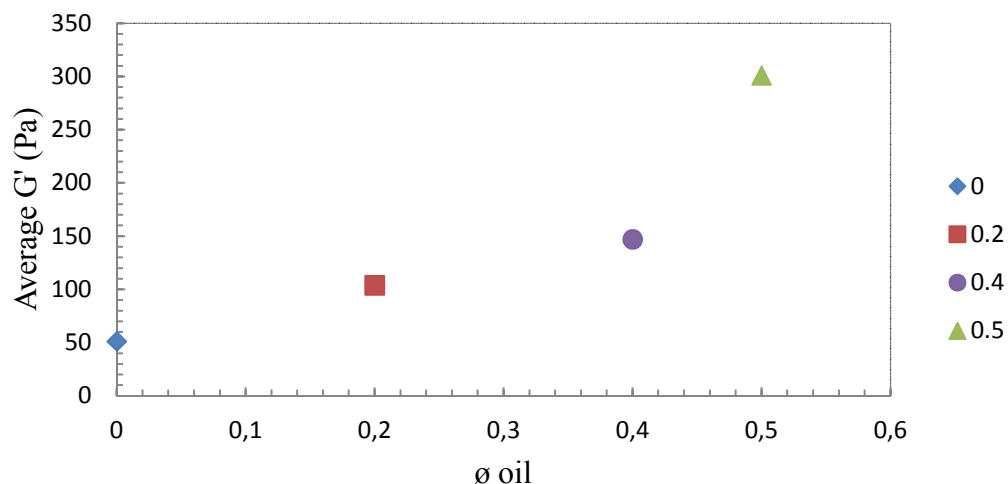


Figure 5.12. Modulus storage average  $G'$  in function of different concentrations of oil for the same sample of laponite 2.2 wt% at 0.002 M.

It is shown that  $G'$  increases at higher concentration of volume oil exponentially. The explanation for this result is that at higher oil volume fraction it increases the number of drops in the sample. Consequently, increasing the elasticity of the material.

#### 5.2.5.5.5. Breakdown test

Figure 5.13 shows the time-dependent structural and mechanical changes occurring in a gel subjected to a jump in shear rate, after a period of rest defining the initial state, and then to an interruption of shear, for a different concentrations of laponite and salt.

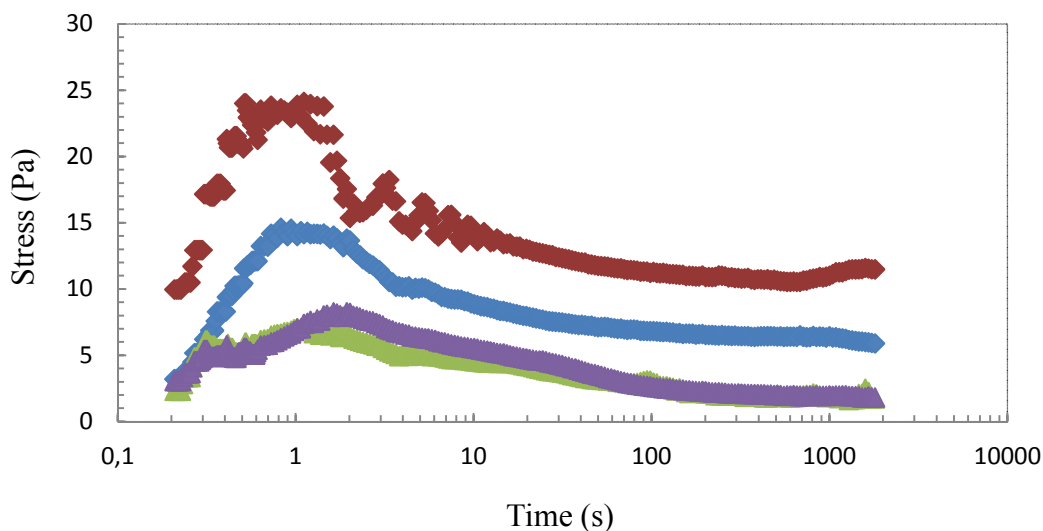


Figure 5.13. Stress response under steady shear rate of  $10\text{s}^{-1}$  for 1,800 sec. Dispersions at different concentration of laponite and different concentration of salt 2.2 wt% at 0.002 M salt ( $\blacklozenge$ ) and 2.4 wt% at 0.01 M ( $\blacktriangle$ ). Emulsions at different concentration of laponite and salt, 2.2 wt% 0.002 M salt ( $\blacklozenge$ ), and 2.4 wt% 0.01 M ( $\blacktriangle$ ). Both at  $\phi=0.20$  oil.

During the unsteady conditions following the application of the jump in shear rate, sample changed from the initial isotropic behaviour to critical strain corresponding to maximum stress. This occurs very quickly. Then, the sample recovers its initial state and remains stable.

As shown in figure 5.13, between dispersion and emulsion at the same concentration of laponite, the maximum stress is higher in the emulsions. In addition, it is observed that at higher salt concentration, the peak of maximum stress is lower.

#### 5.2.5.5.6. Recovery test

Figure 5.14 shows the results of the recovery test for dispersions and emulsions for a different laponite and salt concentration. In the recovery test, a constant static load is applied to the sample.

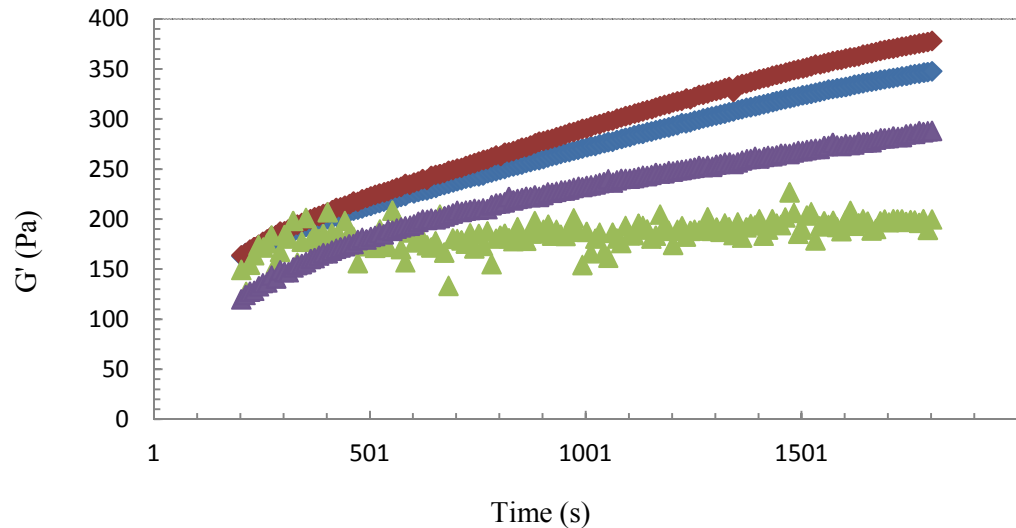


Figure 5.14.  $G'$  response under steady shear rate of  $300 \text{ s}^{-1}$ . Dispersions at different concentration of laponite and different concentration of salt 2.4 wt% at 0.002 M salt ( $\blacklozenge$ ) and 1.35 wt% at 0.01 M ( $\blacktriangle$ ). Emulsions at different concentration of laponite and salt, 2.4 wt% 0.002 M salt ( $\blacklozenge$ ), and 1.35 wt% 0.01 M ( $\blacktriangle$ ). Both at  $\phi=0.20$  oil.

As shown in figure 5.14  $G'$  increases over time, while the shear rate is applied, until finally reaching a steady state, when the shear ceases called the recovery state.

The dispersions and emulsions at higher salt concentration show a higher  $G'$  when the sample recovers its initial state. If it is compared to the dispersions and emulsions at the same concentration of laponite and salt, the emulsion shows a higher  $G'$ .

### 5.3. Conclusions

Experiments have demonstrated that laponite RD dispersions can be used to establish emulsions; therefore, they erect a physical barrier between drops retarding coalescence.

Also investigated was the stabilisation for different types of oils where bromohexadecane was chosen, which has a density similar to water, and according to the results, creaming is avoided.

In emulsions and dispersions established by laponite the viscosity depends on laponite and salt concentration. Viscosity increases slightly from aging. Emulsions and dispersions containing laponite behave as non-Newtonian fluids. Samples show shear thinning, which is

the tendency of some materials to decrease in viscosity when driven to flow at high shear rates. The viscosity of thixotropic dispersions and emulsions (gels of fluids which have viscosity that decreases when a stress is applied), is higher than the viscosity of the dispersant liquid due to the presence of an internal structure.

Oscillatory measurements were used to investigate the viscoelastic properties  $G'$ ,  $G''$ ,  $\tau$  and  $\tan \delta$  when strain or frequency were applied. LVR was identified by the measurements obtained from strain sweep test (strain applied). Frequency sweep test permits one to obtain  $G'$  average of all the samples analysed. Measures show  $G'$  average depends of laponite concentration according to the phase diagram at high pH for laponite dispersions. In addition, the relation between  $G'$  average and oil volume fraction,  $\phi$  was demonstrated.

Rheometric measurements of the thixotropic behaviour of laponite dispersions and emulsions were studied.

Breakdown test shows the disruption of network particles in achieving the maximum stress generated by shearing. The results for different dispersions and emulsions show that the maximum stress applied is higher in emulsions for dispersions and emulsions with same laponite and salt concentration. This is due to the network formed in emulsions and dispersions, where emulsion's networks are harder to disaggregate.

Recovery test which takes one place after the system is left to rest after breakdown, shows the same results as the Breakdown. Emulsions show higher  $G'$  when the sample is recovering where the continuous aggregate network is re-established.

## 6. SAFETY INSTALLATIONS

Safety in chemical plants is a very important matter to take into account when the plant is designed. The safety within a plant is designed according to Work safe's National Standard for plant regulation established in Australia (ref. 25). The Safety standard was compared with guidelines applied in Spain 96/82/CE (ref.26) In addition, to determinate the necessity of doing a analysis of the risk, *Instrucció 11/2010 SIE* was consulted (ref. 27) which is applies in Catalonia for the Chemical industry.

### 6.1. Identification hazardous zones

The plant does not have a hazardous zone. As already mentioned, all the materials stored in the tanks are classified as Class D. Table 6.1 shows the most important characteristics.

Table 6.1. Characteristics of raw compounds.

	Dow Corning 200 350 cst	Pure Thix HH
Flash point	350°C	109°C
Flammability	Yes	Yes
Liquid Class	D	D
Oxidizing	Yes	Yes

According to Work safety National Standard, they are not considered as hazardous materials, even though they are flammables. The products stored in the warehouse in containers, such as bags or bottles, are not considered to be hazardous, although, workers must abide by handling protocols and the use of compulsory personal protection.

Dow Corning 200 350 cst (type of silicone) and Pure Thix HH (1,3-butylene Glycol (and) water (and) Polyether-1) are non-flammable liquid compounds (the compounds do not contain R10 or/and R11, R12), following the MSDS from *El Ministerio Nacional de Seguridad e Higiene en el Trabajo* (ref. 28) *Real Decreto 1272/2008* (ref.29) and REACH (ref. 30).

However, the Dowicil 200 is toxic to aquatic media (R52-53) and flammable (R11), as reported by the MSDS to *El Ministerio Nacional de Seguridad e Higiene en el Trabajo* (ref. 28) Even if it is categorized as a hazardous compound, it does not require an analysis of the

risk because it is a solid material stored in 5kg-bags in the warehouse in agreement with *Instrucció 11/2010 SIE* (ref. 27).

The agitation tank AT-201, however, could be considered hazardous. This facility does not work under dangerous conditions, but the existence of multiple batches in progress at a given time presents numerous opportunities for the process operator to make errors, such as charging a material in the wrong batch. If the error is not recognised quickly, so that the proper charge can be made, the error is detrimental to the batch to which the charge was supposed to be made.

Such errors usually lead to an off-specification; the consequences could be more serious and could result in hazardous conditions, but it is not the case due to the materials are not considered hazardous and they do not have reactivity between each others.

Therefore, to avoid this possible situation, off-specification a good planning and organisation are required.

## **6.2. Protection in overpressure/vacuum equipment**

In the plant, all equipment works at atmospheric pressure. Nevertheless, in the loading and unloading processes, there could be situations of overpressure or vacuum. To prevent this, and to avoid the possibility of oxidation and to keep the purity in closed tanks T-102, T-103 and T-104, blanketing systems are installed.

## **6.3. Personnel protection**

The operators who gain access to the facilities have to wear the statutory equipment. This equipment is safety boots, helmet, gloves and glasses.

The pipe lines which are at a temperature of above 60 °C, (temperature that could cause burns) must be protected by insulation. This line corresponds to De-Water supply.

The operators in charge of the manipulation of materials, that are stored in bottles or bags, must follow the instructions specifically mentioned in the MSDS for each compound, and must wear suitable protective gear.

Also, eye baths are installed within areas of risk whereby the distance between each is no further than 20 meters. All of the eye baths are supplied with water.

#### **6.4. Protections measures fire-prevention**

The protection system of the plant was designed according to guidelines from *Real Decret 2267/2004* (ref. 31) and the guidelines applied in Australia, as already stated. This plant is considered as type C, an industrial facility located in a building. The whole facility is considered fire area.

The plant has foam dispensers installed, where the foam flow required in storage tanks T-102 and T-103 is 4 litres per minute per meter square of surface and the minimum time of application is 25 minutes. The agitation tank also uses a foam extinguisher. They will be located in accessible place and be easily visible.

In addition, fire hydrants are installed strategically in the plant. These fire hydrants have to be properly connected to net water and water supply. Fire hydrants are the 45 mm type and are located over a rigid support, whereby the centre has to be at a height of 1.5 metres. The material lines are made of steel and only used for fire protection. The minimum flow is 12m<sup>3</sup>/h and the distances between each other are 40 m.

The emergency lights are located in the control room of the plant. Therefore, in case of fire, the operators working in the plant can take the proper actions to avoid dangerous consequences. This system has its own energy supply and would be turned on automatically in case of a 70% breakdown of voltage supplied to the plant.

All emergency exits will be properly signposted, as well as facilities related to fire protection. All equipment has been designed according to proper codes for tanks, pipes, etc; therefore they are protected against fire and from the electrical network.

## **7. ENVIRONMENT IN THE DESIGN OF THE FACILITIES**

### **7.1. Pollutants**

It is important to note that during the normal operation of the plant, air emissions of greenhouse gases are not generated. As follows, the pollutants generated by the plant are explained.

#### **7.1.1. Liquid waste**

Every time the agitation tank AT-201 is cleaned, dirty water is generated. This water cannot be flowed directly without a previous treatment. Therefore, the water is stored in a tank and sent to a wastewater plant. It must be taken into account possible spills related to storage tanks. Tanks have spill containments. Firstly, spills will be treated according to safety data sheet of each compound and sent to the treatment plant or stored in special containers.

#### **7.1.2. Solid waste**

No solid waste is produced during the production process; the only solid residues to be considered are the ones that can be found at the bottom of the tanks during the cleaning process. These compounds will be treated in the proper facilities. In addition, it must be taken into account possible spills of raw material in powder state. The procedure will be the same as the one stated in the liquid waste.

#### **7.1.3. Noise generation**

The only sources of noise pollution inside the plant are produced by the pumps. In case that during the operation time, pumps would produce more than 80 dB, the maximum amount of decibels allowed by law, the pumps must be insulated to ensure that the law is upheld.

## **7.2. Consumption of Energy and Natural Resources**

This plant does not require a great amount of natural resources neither the energy consumption. Natural resources used in the plant are listed below:

- Tower water is used in cooling jacket of the AT-201.
- Electricity required for the whole plant.

## **8. MAINTENANCE OF THE INSTALLATION**

The plant must be designed for maximal operative life. To keep the plant in proper conditions the maintenance of the installation must be considered. All equipment in the plant has to be accessible for repair and maintenance. Dynamic equipments and accessories, pumps, valves sampling, etc, must be accessible too. Also, any spills which could occur must be taken into account. Spills must go to containers with periodic checks of the storage installations.

This chapter explains the main operations of corrective maintenance, as well as preventative procedures.

### **8.1. Corrective maintenance**

This type of maintenance involves stocking up replacements for all equipment and accessories of the plant and proper logistic services to avoid problems with the delivery of replacements.

The main important corrective maintenance procedures are as follows:

- Replacement of valves which have become loose.
- Replacement of instruments which do not work properly.
- Repair of equipment with fissures.
- Repair broken-down equipment.

### **8.2. Preventive maintenance**

The care and servicing for the purpose of maintaining equipment and facilities in satisfactory operating condition by providing for systematic inspection, detection, and correction of incipient failures, either before they occur or after they have occurred.

#### **8.2.1. Preventive maintenance related to time**

- Every 6 months the storage and final product tanks (T-101, T-102, T-103 and T-104) will be inspected and cleaned.

- All valves will be inspected periodically.
- Check for all safety equipment, as well as, the transmitters and the indicators.

Equipment is checked and tared by an authorized inspector or by a collaborating expert

- Replacement of lubricant in dynamic equipments every 6 months.
- Lubricate the bearing of dynamic equipments every 6 months.
- Revision of the mixer of the agitation tank AT-201 which is specified by the manufacturer.

### **8.2.2. Preventive maintenance related to state**

The care and servicing by personnel for the purpose of maintaining equipment and facilities in satisfactory operating condition by providing for systematic inspection, detection, and correction of incipient failures, either before they occur or before they evolve into major defects.

According to guidelines in Australia, and according to “*Real Decreto 668/1980*” (ref. 32) and MIE-APQ-1, Guidelines for Storage for Chemicals Products”, it has been decided to inspect each storage zone every 5 years. All duties required for maintenance every 5 years are as follows:

- No modifications of anything that could change the safety level that had been approved.
- The products and the capacities must be the same as the initial project.
- State of pipes, cementation and drains must be checked.
- Electrical continuity must be checked in all the facility.
- Sight inspection of the walls of tanks.
- Must be checked: fire- extinguishers, pumps and fire hydrants.

### **8.3. Predictive maintenance**

Techniques which help determine the condition of in-service equipment in order to predict when maintenance should be performed. This approach offers cost savings over routine or time-based preventive maintenance, because tasks are performed only when warranted.

- Static equipment: to keep the equipment in working order is necessary to check the thickness by non-destructive assay, such as, penetrating liquids for pipes and tanks. It is important to check the insulation state in tanks and pipes and the metallic parts of them and also the possible fissures, escapes, etc. These inspections will be done by authorised inspectors during the whole life of the equipment.
- Dynamic equipments: to keep the equipment in working order it is necessary to check vibrations, field observations as well as checking the services parameters such as pressure, temperature, etc. In addition, it is necessary to analyse the lubricant and check the temperature of bearing.
- Instruments: the plant must have a predictive maintenance plan to check the safety valves, transmitters, etc.
- Electrical equipment will be checked within the instruments such as thermographers in electric boards, as well as the analysis of lubricants used in transformers, etc.

## **9. MANUAL OPERATIONAL**

This chapter contains the standard operating procedures and emergency instructions. The standard operating procedures outline those procedures required for normal operation of the plant, including procedures for start-up and shutdown and the schedule of the plant.

### **9.1. Plan production and schedule production**

#### **9.1.1. Introduction**

This plant is considered a multiproduct or specialty plant because it is capable of producing small amounts of a variety of products.

In this kind of plants, the margins are usually high, so factors such as energy cost are important but no life-and-death issues. As the production amounts are relatively small, it is not economically feasible to dedicate processing equipment to the manufacture of only one product. Instead, batch processing is utilized so that several products can be manufactured with the same process equipment. The key issue in such plant is to manufacture consistently each product in accordance with its specifications.

In a batch process, the conditions with the process are continually changing. The technology for making a given product is contained in the product recipe that is specific to that product. Such recipes normally state the following:

- Amount of raw material: are the chemical compounds needed to make the product.
- Processing instructions: is what must be done with the raw material to obtain the desired product.

Sometimes, the term recipe is used to designate only the amount of raw material and other parameters to be used in manufacturing a batch. Although, appropriate for some batch processes, this concept is far too restrictive for others.

In this plant, the concept of flexible batch is applied: both, the formula and the processing instructions can change from batch to batch. The recipe for each product must detail both

the raw materials required and how conditions within the batch must be sequenced to produce the desired product. Flexible batch is by far the most difficult to automate and requires a far more sophisticated control system.

**9.1.2. Batches and Recipes**

Each batch of product is manufactured in accordance with a product recipe, which contains all information required to result in a batch of the product. For each batch of product, there will be one and only one product recipe.

In this plant, the batches in progress do not use the same recipe. The existence of multiple batches in progress at a given time presents numerous opportunities for the progress operator to make errors, such as charging a material to the wrong batch.

However, this situation can be avoided by labelling every batch of product; each batch is assigned with a unique identifier called the batch ID. In table 9.1 is shown an example of the batch ID. Product A corresponds to sunscreen.

Table 9.1. Batch ID.

	<b>Product A</b>	<b>Product B</b>	<b>Product C</b>
<b>Batch 1</b>	ID 1A	ID 1B	ID 1C
<b>Batch 2</b>	ID 2A	ID 2B	ID 2C

**9.1.3. Routing and production monitoring**

Product runs (also called process orders) are scheduled by the plan production, where a stated quantity of a given product is produced.

In executing a production run, the following issues must be addressed, as it is shown in figure 9.1.

- Processing equipment must be dedicated to making the run: this plant has two runs which are in progress at a given time. The maximum numbers of runs simultaneously in progress are two and they are routing which involves to determine which process will be used for each production run.

- Raw material must be utilized: when a production run is scheduled, the necessary raw materials must be allocated to the production run. As the individual batches proceed, the consumption of raw material must be monitored for consistency with the allocation of raw materials to the production run.
- The production quantity for the run must be achieved by executing the appropriate number of batches.

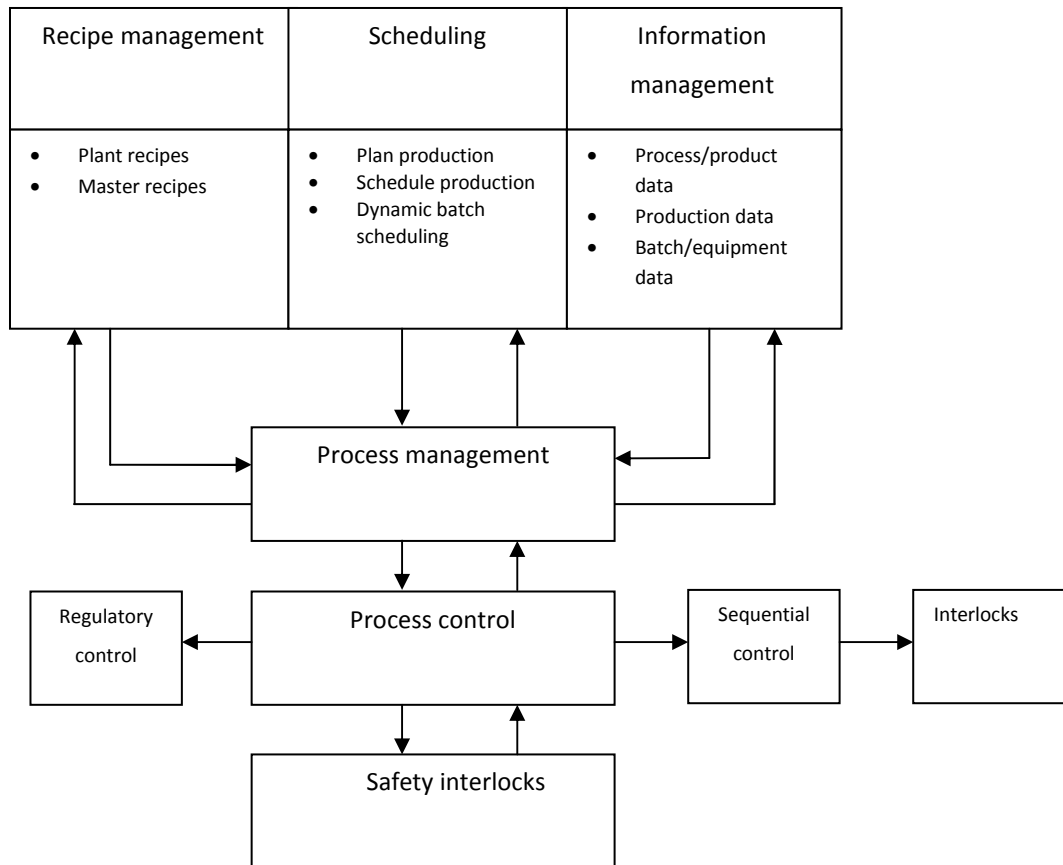


Figure 9.1. Batch control overview.

#### 9.1.4. Production Scheduling

Production scheduling refers to scheduling runs also called long-term schedule. The long-term scheduling is basically material resources planning (MRP) whose main points are the following:

- Forecasting: orders for long-delivery raw materials are based on the forecast for the demand for products. In this case, all the products increase their sales during spring and summer.
- Plant locations and capacities: the plant is located close to the bottling plant. This way, transportation costs are reduced.

As already mentioned, these kinds of products have to pass an exhaustive quality control that takes several months. For this reason, the batches are rotating.

Table 9.2. shows the schedule planning for 3 months.

<b>Month 1</b>				
<b>Batch</b>	<b>Week 1</b>	<b>Week 2</b>	<b>Week 3</b>	<b>Week 4</b>
<b>1</b>	Product A	Product A	Product A	Product A
<b>2</b>	Product B	Product B	Product C	Product C
<b>Month 2</b>				
<b>Batch</b>	<b>Week 1</b>	<b>Week 2</b>	<b>Week 3</b>	<b>Week 4</b>
<b>1</b>	Product B	Product B	Product B	Product B
<b>2</b>	Product A	Product A	Product C	Product C
<b>Month 3</b>				
<b>Batch</b>	<b>Week 1</b>	<b>Week 2</b>	<b>Week 3</b>	<b>Week 4</b>
<b>1</b>	Product C	Product C	Product C	Product C
<b>2</b>	Product B	Product B	Product A	Product A

For this chapter, all the information was taken from ref Perry's (ref. 33)

## 9.2. Start-up

Along these lines, all the steps to start-up the process of plant are explained. It must be taken into account that only the process for production of sunscreen in agitation tank AT-201 is explained. However, for product A and B the procedures are very similar.

This is a batch plant; all the procedures involved are explained sequentially.

1. Check all the control system to ensure that it is working properly.
2. Check that all the manual valves are closed.
3. Check De-water net supply is working properly.

4. Check all raw compounds are available and have the quality required, through quality control processes.
5. Check pumps are turned off.
6. All process valves must be closed.
7. Check schedule to know which raw materials according to the recipe, in this case, sunscreen recipe (as shown in chapter 4), and batch must be used. An ID is set, as an example; ID1A means product A, sunscreen, and agitation tank AT-201.
8. Check the proper agitation tank has been cleaned. It is required to clean the equipment after every use, for hygienic and purity reasons.
9. An operator opens V-101 and V-102 from the plant to fill Tank T-101 with De-water. At the same, the generator G-101 is activated from the control room.
10. When T-101 achieves the proper level indicated by LIAS-101, LCV-101 closes. Then, the same the operator closes V-101 and V-102 manually.
11. Meanwhile other operators carry all the solids and liquids compounds required by the recipe from the warehouse to agitation tank AT-201. As already mentioned, to transport these compounds the operator uses a wheelbarrow. The compounds are lifted to the level of the walkaround, located on the top of the vessel using an automatic pulley.
12. When De-water achieves to 60°C, the generator is turned off, the valves V-103, V-104, V-105, V-106, V-107, V-108 and V-501 are opened and the fluid goes from T-101 to AT-201. When it achieves the proper level to turn on the loading pumps P-101A/B, the pumps are turned on by an operator, turning on only one pump, in this case P-101A.
13. At the same time that P-101A turns on, the inlet of De-water, into the AT-201 by FICQAS-501, is controlled and quantified in the control room during the loading of AT-201.
14. When the level of fluid in T-101 and the inlet of the same fluid decreases from the set point fixed, the controls act closing valve FCV-101 and turning off P-101A. This way, the required quantity of water established by the recipe is obtained. The excess of liquid remains inside the pipes avoiding the cavitation of the pumps.
15. When the agitation tank is filled with De-water, valve V-501 is closed manually.
16. Then, the solid compounds of Phase A (stabilizers) are added as stated in the recipe. Two operators have to carry all compounds to AT-201 and check again that the compounds and the quantity of the compounds is correct, as shown in chapter 4. The compounds are added using a feed hopper that is situated on the top of the same vessel.

17. While the compounds are added, the motor of the mixer M-501 is turn on manually, fixing the speed to that required for the process (500 rpm).
18. When all the compounds of phase A are added, and the dispersion is formed after the mixing time (30 minutes), phase B starts to be added.
19. After adding phase B (citric acid) is added, V-506 is opened to allow the inflow of cooling water into the jacket of the agitation tank, beginning the cooling process. At that point, the shear speed is changed (increased until 700 rpm) according to the recipe.
20. When the cooling process starts, phase C is added (Dow Corning, Titanium dioxide, Glycerin).
21. The operators add manually the solid compounds corresponding to phase C.
22. The valves V-201, V-202, V-203 V-205 V-207, V-208, V-502 and V-510 are opened.
23. P-201A is turned on and Dow Corning goes into AT-201. R-501 (Ratio control) controls the inlet of Dow Corning into AT-201 by FCV-502. FIC-501 sends an input to R-501 (Ratio control) and R-501 sends an input to FICQAS-502. Then, FICQAS-502 sends an output to FCV-502 to manipulate the inlet of Dow Corning according to the recipe.
24. FICQA-202 measures the inlet of Dow Corning. When the quantity of Dow Corning needed in the recipe is accomplished, FCV-202 is closed.
25. Finally, phase D is added (Pure Thix HH and Dowicil 200). The operators add the Dowicil 200 into the AT-201 while Pure Thix HH is added following the same procedure as Dow Corning (opening valves V-301, V-302, V-303 V-305 V-307, V-308 and V-503 and V-511 are opened) and turning on P-301A.
26. R-502 (Ratio control) controls the inlet of Pure Thix HH into AT-201 by FCV-503. FICQA-502 sends an input to R-502 (Ratio control) and R-502 sends an input to FICQA-503. Then, FICQA-503 sends an output to FCV-503 to manipulate the inlet of Pure Thix HH according to the recipe.
27. FICQA-301 measures the inlet of Pure Thix HH. When the quantity is accomplished according to the recipe FCV-302 is closed.
28. While all the compounds are added, the agitation tank is kept mixing. When the temperature of the mixture is at temperature room, the inflow of cooling water is cut off.
29. At the same time, the motor of mixer M-501 is turned off from control room.
30. An operator opens V-505, V-506, V-508 and V-509, turns on P-501A and the product goes to the final product tank T-104 and FICQA 504 quantifies the amount of the final product.

31. When the level of fluid in AT-501 and the inlet of the same fluid decreases from the set point fixed, the controls act closing valve FCV-504 and turning off P-501A. This way, the required quantity of water established by the recipe is obtained. The excess of liquid remains inside the pipes avoiding the cavitation of the pumps.
32. Every month, the final product is unloaded. To unload the final product, V-401 is opened and the product is transferred to another tank which is not in the battery limits of this project.

### **9.3. Emergency shutdown**

#### **9.3.1. Failure of energy supply**

All dynamic equipments are activated by electric dynamic motors, therefore in case of blackout, the shutdown of the whole plant will occur. The dynamic equipments of the plant are the pumps and the mixer. In this case, it is very important to have a backup system to generate enough electricity to run the basic elements of the plant and thus, end up in a position to stop. Also, this plant has static equipment which needs power supply: the electric coil in T-101.

As already stated, all the dynamic equipments have a control to turn off the equipments properly.

#### **9.3.2. Failure in the instrument air supply**

A failure in the air supply instruments involves a loss of control over the plant, which can cause off specification products. Therefore, it is required a second auxiliary air system to move the electroneumatic valves.

The most important valves in the process are the valves which control the inlet and outlet of nitrogen (blanketing system) keeping a nitrogen atmosphere in the tanks (T-102, T03, T-104)

and the valves which control the amount of the each raw material following the recipe. In case of fail, it causes off specification of the final product.

### **9.3.3. Failure in cooling water supply**

Failure in cooling water supply causes off specification as explained above, because the recipe must be followed in detail. Fortunately, the process does not involve chemical reactions, so a possible thermal runaway is not feasible.

## **10. PROFITABILITY ANALYSIS**

The profitability analysis of the plant is one of the most important sections of this project, if the profitability does not indicate a return of investment in a short period of time; it is possible that the plant may never be built.

In this chapter, the results of the economic viability of the project, cash flow and the global assessment of the investment are shown.

### **10.1. Starting data**

Despite this project only studies the production of sunscreen; this plant produces 2 more products A and B. In order to conduct a proper economic study, the three products and the two equal process lines are taken into account.

The profitability only applies for the facilities involved in the battery limits, the storage tanks of the raw materials and the storage tanks of the final products, and the agitation tank of the two lines of process. Neither the loading and unloading stations, nor all the facilities related to them, nor the building of the plant are taken into account.

### **10.2. Project implementation budget**

The project implementation budget involves the calculations of the design, the construction and the start up of the facility. The total cost of the facility is obtained by calculating the estimated cost of the equipment and fixing the characterization of the facility.

#### **10.2.1. Estimated cost of the equipment**

The estimated cost of the equipment is calculated using graphics (ref. 34). However, these costs are not updated. The update is done using the equation (10.1) and the index of industrial price (IPRI) provided by *El Instituto Nacional de Estadística* (Institute National of Statistics).

$$\text{Updated cost} = \text{Referenced cost} \frac{IPRI_{2011}}{IPRI_{reference}} \quad (10.1)$$

Where, the reference year taken is 1982, the IPRI is 43.3. In April 2011, the IPRI is 101.5 for industry of personal products (ref. 35).

In appendix 5, one can see the results of the update cost of the equipment. The total cost of equipment is shown in table 10.1. The cost of each equipment can be found in appendix 5.

Table 10.1 Total cost of the equipment.

Facility	Number of equipment	Updated Costs (\$)
Pump P-101 A/B	2 (1)	303,797
Pump P-102 A/B	2 (1)	300,984
Pump P-103 A/B	2 (1)	295,358
Pump P-501 A/B	2 (1)	306,610
De-water Tank T-101 (2)	2	113,924
Storage Tank T-102	2	53,914
Storage Tank T-103	2	46,882
Agitation Tank AT-501 (3)	2	41,819
Storage Tank T-104	2	70,323
<b>Total (4)</b>	<b>26</b>	<b>1,533,611</b>
<b>Total (AUD\$)</b>		<b>1,464,767</b>

(1) Note that the total pumps are four (2 pumps A and 2 pumps B).

(2) The cost includes the electric coil and the tank.

(3) The cost includes the mixer and the agitation tank.

(4) 1 dollar (\$) is 0.955 Australian dollars (AUD\$).

The total cost in equipment includes the two process lines which are identical. This two process lines involve the agitation tanks, the pumps and the storage tanks.

### 10.2.2. Estimated cost of the facility

Using the equipment costs, the total installation cost is calculated, taking into account its characteristics found in table 10.2.

Furthermore, the indirect costs and unforeseen expenses are fixed at a 29% and 14% of the direct costs, respectively.

Table 10.2 Characterization of the facility.

<b>Parameters</b>	<b>Type</b>
Basic Equipment Assembly	Average
Foundations and Structures	Average (carbon steel)
Piping	Low liquids and solids
Power and Lightning	Low
Instrumentation	Liquids
Other factors not accounted	Complicated process
Buildings	Inside Equipment

### **10.3. Income statement account**

Based on the income statement account, a prediction of the annual profit and loss is generated. In order to calculate this profit and loss, the income and annual costs derived from the unit operation are taken into account.

#### **10.3.1. Annual income**

The income generated by the plant belongs to the sales of the 3 final products produced in the plant. The retail price for every product can be found in table 10.3.

Table 10.3. Sale cost of the products.

<b>Product</b>	<b>Production (Tm/year)</b>	<b>Selling cost (AUD\$/Tm)</b>	<b>Income (AUD\$)</b>
Sunscreen	500	7,500	3,750,000
A	500	7,500	3,750,000
B	500	7,500	3,750,000
<b>Total</b>	<b>1,500</b>	<b>22,500</b>	<b>11,250,000</b>

#### **10.3.2. Annual costs**

The expenses from the plant are established by the consumption of ancillary services, raw material costs, personnel costs, installation costs and maintenance costs. In table 10.3, the total costs of the already listed expenses can be seen. For more details, check annex 5.

Table 10.3. Total annual cost.

<b>Expenses</b>	<b>Cost (AUD\$)</b>
Utilities	3,150,851
Raw material	4,541,100
Human Resources	1,594,440
Facilities	160,612
Maintenance	104,402

Note that the raw material is calculated taking into account the raw materials for sunscreen. However, to simplify the calculations, its considered that the three products use the same raw materials.

#### **10.4. Global investment evaluation**

To determinate the profitability of the project, the global evaluation of the investment must be conducted. The profitability of the project is measured through Cash flow, NPV (Net Present Value) and IRR (Internal Rate of Return). The calculation details are found in annex 5.

##### **10.4.1. Calculation of Cash flow**

To calculate the Cash flow; all operating costs, recovery of plant and initial investment must be taken into account. Note that the period of study is 10 years.

First of all, the Cash flow is calculated, although the other factors are based on it. As follows, the used equations are shown.

$$PBT = Income - Expenses - Inventory \quad (10.2)$$

$$Taxes = (PBT - Amortization) \cdot SRIT \quad (10.3)$$

$$Cash\ flow = PBT - Capital - Taxes \quad (10.4)$$

$$Amortization = \frac{TCI}{lifetime} \quad (10.5)$$

Where PBT is the *Profit Before Taxes*, SRIT is the *Statutory Rate of Income Tax*, fixed at 30%, TCI is the *Total Cost Investment*, and the lifetime is ten years.

Once, the *Cash flow* is done, the next step to follow is to calculate the cumulative cash flow. The investment returns is the time from the decision to proceed until cumulative cash flow becomes positive, as one can see in figure 10.1. In this case, the time to recover the initial investment is 5 years.

Figure 10.1 shows the results for accumulate cash flow, using the data for cash flow accumulative and the recovery of the investment takes place in 5 years.

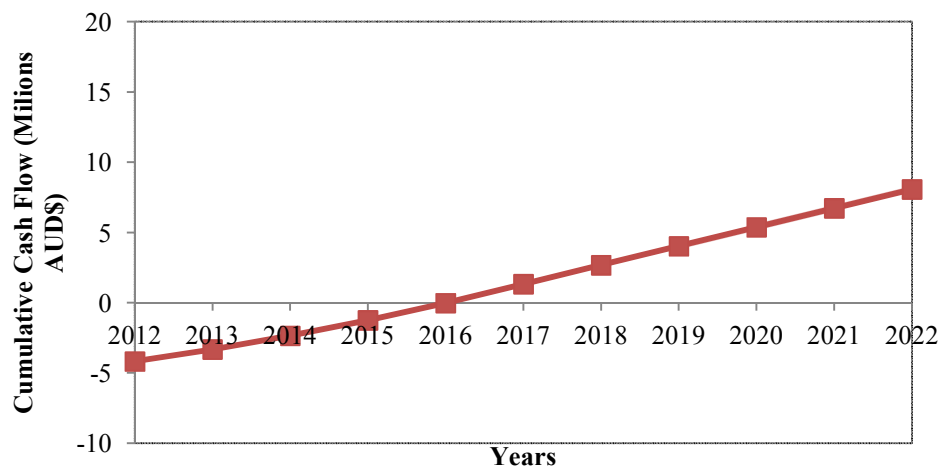


Figure 10.1 Evolution of Cash flow accumulative for the amortization years.

**10.4.2. Calculation of Net Present Value (NPV)**

NPV, net annual value, is the gross amount that can be expected to be rented from year to year.

$$VPN = \sum_{t=1}^n \frac{Cash\ Flow}{(1+k)^t} - I_0 \tag{10.6}$$

Where, Cash flow is the revenue or expense stream that changes a cash account over a given period, t, n is the number of periods, I<sub>0</sub> is the initial investment and k is the interest applied, fixed at 9%.

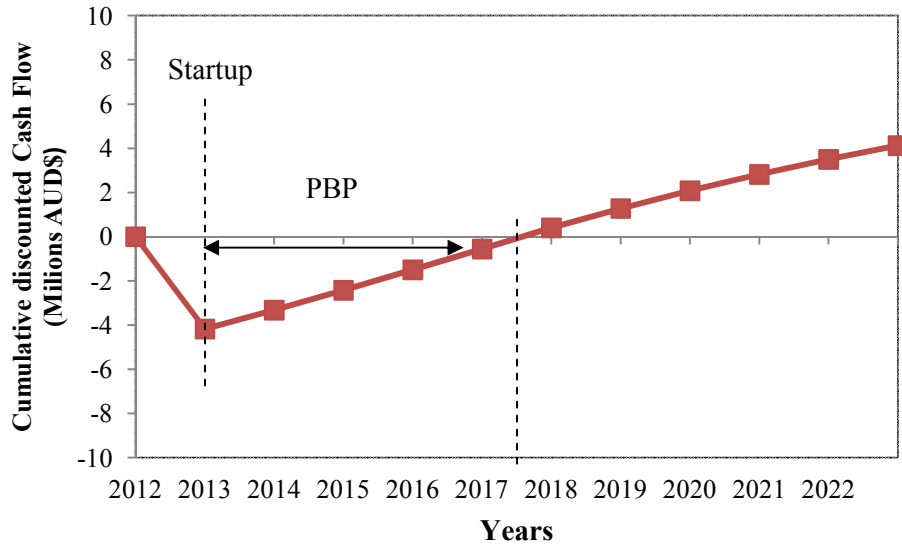


Figure 10.2. Evolution of the NPV over the years of the profitability analysis.

**10.4.3. Calculation of Internal Rate of Return (IRr)**

IRR (Internal Rate of Return) is the rate that will discount all cash flows to a net present value of zero. In this case, the IRR is 32.8%.

$$NPV = \sum_{t=1}^n \frac{Cash\ Flow}{(1+k)^t} - I_0 = 0 \tag{10.7}$$

**10.4.4. Pay back period (PBP) and discounted break-even period (DEBP)**

*Pay back period* (PBP) is the time that must elapse after start up until cumulative cash flow data repays the fixed capital investment. Therefore, in this case, the PBP is 4.5 years. In figure 10.2, one can see the PBP.

$$PBP = \frac{TCI}{Profit} \tag{10.8}$$

*Discounted break-even period* (DEBP) is the time from the decision to proceed, in this case to build the plant, until discounted cumulative cash flow becomes positive. In figure 10.2, one can see that DEBP is 5.5 years.

### **10.5. Conclusions of profitability analysis**

After conducting the economic study of the sunscreen production plant, and other personal care (skin care) products for a period of 10 years, it can be concluded that the project is economically viable. As it is shown in the initial investment study, the investment can be recovered in 5 years, when the plant is still at 95% of its production capability. The values obtained for the NPV and IRR are 4.12% and 32.7%, respectively.

## **11. REFERENCES**

(ref. 1) F. Pignon, A. Magnin, and J. Piau, *Thixotropic behavior of clay dispersions: Combinations of scattering and rheometric techniques*, Laboratoire de Rheologie.

(ref.2)<http://theaustralian.com.au/business/sunscreen-maker-eyes-worldmarkets/storye6frg8zx-1225815367373>

(ref. 3) J. Chem, *Emulsions S.U. Pickering*. Soc. 91 (1970)200

(ref. 4) <http://www.wisegeek.com/what-is-the-history-of-sunscreen.htm>

(ref. 5) Shaath, Nadim A; Lowe, N. J; Pathak, Madhu, *Sunscreens: Development, Evaluation, and Regulatory Aspects*, A.Vol: 15 Edition: 2nd ed., rev. and expanded. ISBN: 9780824793067 Date: 1997

(ref. 6) <http://www.sa.gov.au/subject/Business%2C+industry+and+trade>

(ref.7) Info [www.bom.gov.au](http://www.bom.gov.au)

(ref. 8) [http://www.pir.sa.gov.au/minerals/earthquakes/earthquake\\_-\\_adelaide\\_risk](http://www.pir.sa.gov.au/minerals/earthquakes/earthquake_-_adelaide_risk).

(ref. 9) Stephanopoulos, G., "Chemical process Control. An Introduction to Theory and Practice". Prentice Hall Inc., 1984.

(ref. 10) Donald R. Woods, *Rules of Thumb in Engineering Practice*, 2007.

(ref. 11) [www.terlet.com/Download.aspx?File=225](http://www.terlet.com/Download.aspx?File=225)

(ref. 12) Pär Olsson, *Analysis and modelling of a batch cooling process for cosmetics*, Department of Chemical Engineering, Lund Institute of Technology, January 2005

(ref. 13) Mason, T., J. Bibette, and D. Weitz, *Yielding and flow of monodisperse emulsions*. Journal of colloid and interface science, 1996. **179**: p. 439-448

(ref. 14) Pickering, S.U., *Emulsions*. J. Chem. Soc, 1907. **91**(2001): p. 2021.

- (ref. 15) Binks, B. and S. Lumsdon, *Pickering emulsions stabilized by monodisperse latex particles: Effects of particle size*. Langmuir, 2001. **17**(15): p. 4540-4547.
- (ref. 16) Tsugita, A., et al., *Studies on O/W emulsions stabilized with insoluble montmorillonite-organic complexes*. Journal of colloid and interface science, 1983. **95**(2): p. 551-560.
- (ref. 17) Abend, S., et al., *Stabilization of emulsions by heterocoagulation of clay minerals and layered double hydroxides*. Colloid & Polymer Science, 1998. **276**(8): p. 730-737.
- (ref. 18) Lagaly, G., M. Reese, and S. Abend, *Smectites as colloidal stabilizers of emulsions:: II. Rheological properties of smectite-laden emulsions*. Applied clay science, 1999. **14**(5-6): p. 279-298.
- (ref. 19) Lagaly, G., M. Reese, and S. Abend, *Smectites as colloidal stabilizers of emulsions:: I. Preparation and properties of emulsions with smectites and nonionic surfactants*. Applied clay science, 1999. **14**(1-3): p. 83-103.
- (ref. 20) Yan, N., M.R. Gray, and J.H. Masliyah, *On water-in-oil emulsions stabilized by fine solids*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2001. **193**(1-3): p. 97-107.
- (ref. 21) Labanda, J. and J. Llorens, *Effect of aging time on the rheology of Laponite dispersions*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2008. **329**(1-2): p. 1-6.
- (ref. 22) A. Ragouilliaux, G. Ovarlez, N. Shahidzadeh-Bonn, B. Herzhaft, T. Palermo and P. Coussot, Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys., 2007, 76, 051408.
- (ref. 23) Pignon, F., A. Magnin, and J.M. Piau, *Thixotropic behavior of clay dispersions: combinations of scattering and rheometric techniques*. Journal of Rheology, 1998. **42**: p. 1349.
- (ref. 24) Mouchid, A., et al., *On viscoelastic, birefringent, and swelling properties of Laponite clay suspensions: revisited phase diagram*. Langmuir, 1998. **14**(17): p. 4718-4723.

(ref.25)<http://www.safeworkaustralia.gov.au/SafetyInYourWorkplace/HazardsAndSafetyIssues/Plant/Pages/NationalStandard.aspx>

(ref. 26) Directiva 96/82/Ce del consejo, de 9 de diciembre de 1996, relativa al control de los riesgos inherentes a los accidentes graves en los que intervengan sustancias peligrosas

(ref. 27) Instrucció 11/2010 SIE, criteris per l'elaboració i l'avaluació de l'informe de seguretat a presentar pels establiments afectats en nivell alt per la legislació vigent en matèria d'accidents greus.

(ref.28)<http://www.insht.es/portal/site/insht/menuitem.a82abc159115c8090128ca10060961ca/?vgnnextoid=4458908b51593110vgnvcm100000dc0ca8c0rcrd>

(ref. 29) Reglamento (CE) no 1272/2008 del Parlamento Europeo y del Consejo, de 16 de diciembre de 2008, sobre clasificación, etiquetado y envasado de sustancias y mezclas, y por el que se modifican y derogan las directivas 67/548/CEE y 1999/45/CEE y se modifica el reglamento (CE) no 1907/2006

(ref. 30) <http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances>

(ref. 31) Real Decreto 2267/2004, de 3 de diciembre, por el que se aprueba el Reglamento de seguridad contra incendios en los establecimientos industriales.

(ref. 32) Real Decreto 668/1980, de 8 de febrero, que aprueba el reglamento de almacenamiento de productos químicos boe de 14-04-80.

(ref. 33) *Perry's chemical engineers' handbook*. 8th ed. / ed, ed. R.H. Perry. 2008, New York: McGraw-Hill.

(ref. 34) Gael D. Ulrich, John Wiley & Sons, A Guide to chemical engineering process design and economics Publicació New York [etc.], cop. 1984

(ref. 35) <http://www.ine.es/daco/daco42/daco423/ipri0312.pdf>

# APPENDIX

## **A1. PIPING DESIGN**

### **A1.1. Basic design**

First of all, speed for flow liquids between 1 and 3 m/s must be fixed. Subsequently, the inside diameter of the pipe is calculated (1.1).

$$Di = \sqrt{\frac{4Q_v}{v_{fixed}\pi}} \quad (1.1)$$

Where,  $Di$  is the inside diameter of the pipe,  $Q_v$  is the volumetric flow of fluid and  $v$  the speed of the fluid.

The conditions of design temperature and design pressure are calculated by equations (1.2) and (1.3).

$$P_{design} = P_{operation} + (0,1 \cdot P_{operation} \text{ or } + 1 \text{ bar}) \cdot \rho \cdot g \cdot h_L \quad (1.2)$$

$$T_{design} = T_{operation} + 20^\circ C \quad (1.3)$$

Where,  $\rho$  is the density of the fluid ( $\text{kg/m}^3$ ),  $g$  is the gravitational constant  $9,81 \text{ (m/s}^2\text{)}$  and  $h_L$  is the height of liquid (m). In this case, 1 bar is chosen and the height of liquid is the diameter of the pipe, which is considered.

According to code ASME section B31.3, the equation to calculate the thickness is:

$$t = \frac{P_d \cdot D}{2 \cdot (S \cdot E - P_d \cdot Y)} \quad (1.4)$$

Where,  $t$  is the thickness of the pipe (m),  $P_d$  is the pressure of design (Pa),  $D$  is the diameter of the pipe (m),  $S$  is the stress of the material (Pa),  $E$  is the efficiency of the pipe and  $Y$  is a coefficient depending on the type of the material.

Then, the standard diameter of pipes is fixed according to the standard code ANSI B36.10. Therefore, the speed flow is re-calculated using the equation, taking into account the standard diameters of inside and outside the pipe.

## **A2. DESIGN OF THE PUMPS**

### **A2.1. Mechanical energy balance**

In this process, there are different pumps in terms of their operations within the plant. Their function is to provide enough pressure to ensure the fluid flows properly since the process works at atmospheric pressure.

The mechanical energy balance is always done in units of liquid height, meter, following Bernoulli's equation (equation 2.1)

$$\frac{P_1}{\rho g} + \frac{v_1^2}{2g} + z_1 + h_b = \frac{P_2}{\rho g} + \frac{v_2^2}{2g} + z_2 + h_L \quad (2.1)$$

Where,  $P_1, P_2$  is the pressure,(Pa), at point 1 and 2 respectively, (Pa),  $z_1, z_2$  is the height of point 1 and 2 with respect to the axis of the pump (m),  $v_1, v_2$  is the speed flow (m/s) at points 1 and 2 respectively, (must be taken into account for calculation of load losses),  $\rho$  ( $\text{kg/m}^3$ ) is the density of process flow,  $h_b$  (m) is the height provided by the pump and  $h_L$  (m) is the total load loss due to friction and accessories.

Some density and viscosity data of the compounds are obtained using the correlations from software distil v.4.1. and the msds.

From this data, we can calculate the Reynolds number using expression (2.2). To calculate the friction factor, the following expressions are used:

$$\text{Re} = \frac{v \rho \cdot D}{\mu} \quad (2.2)$$

To calculate the friction factor, the following expressions are used:

$$f = 0.25 \cdot \left( \log \left( \frac{\frac{\varepsilon}{D}}{3.7} + \frac{5.74}{\text{Re}^{0.9}} \right) \right)^{-2} \quad f = -2 \cdot \left( \log \left( \frac{\frac{\varepsilon}{D}}{3.7} + \frac{2.51}{\text{Re} \cdot f^{0.5}} \right) \right)^{-2} \quad (2.3) \text{ and } (2.4)$$

Where the value of the roughness,  $\epsilon$ , is the carbon steel trade, which is equal to  $2.0 \times 10^{-5}$  m. To calculate the total losses the equation (2.5) and (2.6), (major and minor respectively). Both minor and major losses can be obtained from total friction losses.

$$H_m = f \cdot \frac{L}{D} \cdot \left( \frac{v^2}{2g} \right) \quad H_{ml} = f \cdot \frac{L_e}{D} \cdot \left( \frac{v^2}{2g} \right) \quad (2.5) \text{ and } (2.6)$$

## **2.2. Calculation of NPSH available**

Net Positive Suction Head available ( $NPSH_a$ ) is calculated as follows in the equation (2.7). It is characteristic in centrifugal pumps.

$$NPSH_a = \frac{P_0 - P_{vap}}{\rho g} \pm \Delta z - h_{L(suction)} \quad (2.7)$$

Where:

$P_0$  (Pa): pressure at the surface.

$P_{vap}$  (Pa): vapour pressure of the fluid at working temperature.

$\Delta z$  (m): height difference between both liquid heights.

$h_L$  (suction) (m): total pressure loss in the suction line.

$NPSH_a$  must be equal or greater than the NPSH required value ( $NPSH_r$ ). In practice, the  $NPSH_r$  for operation without cavitation and vibration in the pump is somewhat greater than theoretical. The actual  $NPSH_r$  depends on the characteristics of the liquid, the pump speed, and the capacity and impeller design.

The examples of the calculation can be found in Chapter 4.2., in the sheets of calculation of the pumps.

### **A3. EQUIPMENT DESIGN**

#### **A3.1. Basis for designing the tanks**

To design the tanks, the ASME code section VIII, division 1 is used. These tanks have been oversized by 20% to be prepared for possible increases in production. The final dimensions are shown in their specification sheets in chapter 4.2. of the report. The material of all the tanks is SA 283 A. The preliminary consideration for the design as follows:

- De-water Tank: Tank T-101 has an electric coil to heat the water to 60°C. It has a volume capacity of 1 m<sup>3</sup>, approximately the same of the agitation tank AT-201. During the design of this tank has been taking into account, that height and diameter of this tank are practically the same (relation 1:1), to minimize the number of coils passes.
  
- Storage tanks: Tank T-102 and T-103 and T-104 are storage tanks. Tank T-102 has a volume capacity of 25.1 m<sup>3</sup>, T-103 has a volume capacity of 7.6 m<sup>3</sup> and T-104 has a volume capacity of 122 m<sup>3</sup>, which means that it can storage the raw materials and products for 1 month. To design these tanks has been taking into account the relation  $2H \approx D$ ; height size must be approximately, the double of diameter size.
  
- Agitation tank: The design criteria followed for the agitation tank AT-201 is according to the production of the plant. Being a batch plant, it is fixed at an annual production of 500 tones at 5.34 hours per batch. The volume capacity for AT-201 is 1.1 m<sup>3</sup>.

#### **A3.2. Calculation of the Thickness**

The thickness of equipment has been designed to fit the ASME code section VIII, division 1. The preliminary consideration for the design as follows:

- The material for all the tanks has been SA 385 grade A.
- Welding type is 1 and it is partially X-rayed (efficiency is 0.80).
- All the equipments work at atmospheric pressure.

### **A3.2.1. Lids**

Storage tanks T-102, T-103 and T-104, the De-water tank T-101, and the agitation tank AT-201 have semi ellipsoidal lids with a ratio of 2:1 for the top of the tanks and plain lids for bottom of the tanks. To calculate both lips of the tanks, top and bottom, the equation is used (3.1).

$$t = \frac{Pd \cdot D}{2 \cdot S \cdot E - 0,2 \cdot P} \quad (3.1)$$

Where, t is the thickness of the pipe (m), Pd is the pressure of design (Pa), D is the diameter of the pipe (m), S is the stress of the material (Pa) and E is the efficiency of the pipe.

### **A3.2.2. Walls of the tanks**

Storage tanks T-102, T-103 and T-104 and the De-water tank T-101 have cylindrical shape. The agitation tank AT-201 have 2 shapes. The first part is cylindrical and the second part is troncoconic with an angle of 35° to facilitate the unloading of this product which is considered of medium viscosity. To calculate the cylindrical part and the troncoconic part the equations (3.2) and (3.3) are used, respectively.

$$t = \frac{Pd \cdot R}{S \cdot E - 0,6 \cdot P} \quad (3.2)$$

$$t = \frac{Pd \cdot D}{2 \cdot \cos \alpha \cdot (S \cdot E - 0,6 \cdot P)} \quad (3.3)$$

Where, t is the thickness of the pipe (m), Pd is the pressure of design (Pa), D is the diameter of the pipe (m), R is the radio of the pipe, S is the stress of the material (Pa), E is the efficiency of the pipe and  $\alpha$  is the half of the angle in at the higher vertex.

### **A3.2.3. Weight of the tanks**

First of all, the weight of the fluid is calculated using equation (3.4). Then, the weights of each part of the tank of all the tanks are calculated using equations (3.5-7) according to their shape, (3.5) semi ellipsoidal, (3.6) cylindrical and (3.7) troncoconical.

$$Weight_j = V_i \cdot \rho_{fluid} \cdot g \quad (3.4)$$

$$Weight_j = \frac{\pi(D_o^3 - D_i^3) \cdot \rho_{steel} \cdot g}{24} \quad (3.5)$$

$$Weight_j = \pi(r_o^2 - r_i^2) \cdot L \cdot \rho_{steel} \cdot g \quad (3.6)$$

$$Weight_j = \frac{\pi \left( \left( (R_o^3 - R_i^3) + (r_o^3 - r_i^3) \right) + \left( (R_o - R_i) + (r_o - r_i) \right) \right) \cdot h \cdot \rho_{steel} \cdot g}{3} \quad (3.7)$$

$$Weight_{Total} = Weight_{fluid} + Weight_{tank\ empty} \quad (3.8)$$

Finally, the weights of the tanks are calculated following the equation (3.8). To calculate the total weight of the tanks T-101, agitation tank AT-201 and T-104 the weight of the serpentine coil, the mixer and the mesh must be added.

### **A3.3. Design of jacket of agitation AT-201**

The jacket of the agitation tank has been designed to cool the final product from 60 °C to room temperature (17 °C). Therefore, inside this jacket cooling water flows supplied by another company.

To determinate the configuration of the jacket the following equations are used. Knowing the temperatures of the cooling water (from 20 °C to 45 °C) and the final product (from 60 °C to 17 °C), the exchange of heat and flow of cooling water can be calculated.

As a result, the cooling water required is obtained by the equation (3.9). Finally, Q is calculated for the cooling water, knowing that  $Q_{\text{product}} = Q_{\text{cooling water}}$ .

$$Q = m \cdot C_p \cdot (T_o - T_i) \quad (3.10)$$

Where  $m$  is the flow of cooling water,  $C_p$  is capacity heat of cooling water and  $T_o$  and  $T_i$  are the difference of temperature of the cooling water.  $U_o$ , Global heat transfer is supposed to calculate the required area, A using equation.

$$A = \frac{Q}{U_o \Delta T} \quad (3.11)$$

The wet perimeter is calculated using the equation (3.12), (3.13) and (3.14).

$$A_s = \frac{\Pi D_i^2}{8} \quad (3.12)$$

$$De = 4 \frac{A_s}{P_m} \quad (3.13)$$

$$P_m = D_i + \left( \Pi \frac{D_i}{2} \right) \quad (3.14)$$

Where  $A_s$  is the area in  $m^2$ ,  $P_m$  is wet perimeter of the tub (m),  $D_i$  is the inside diameter (m) and  $Do$  outside diameter of the cooling jacket(m).

Nusselt number is calculated for cooling water (3.15) and for the fluid inside the agitation tank (3.16).

$$Nu = 0.33 Re^{0.6} Pr^{0.3} \quad (3.15)$$

$$Nu \left( \frac{\mu_w}{\mu} \right)^{0.14} = C Re^a Pr^{0.33} \quad (3.16)$$

Before calculating the Nusselt, Re is calculated. To calculate Nu inside the tank the equation (3.16) is used, where C=0.05 and a=0.36 are coefficients which depend on type and size of the agitator.

$$Re = \frac{D^2 \cdot N \cdot \rho}{\mu} \quad (3.17)$$

Where,  $D$  is the diameter of the agitator (m) and  $N$  the agitator speed in rev/s. Then,  $h$  of the fluid inside of the cooling water is calculated using equation (3.18). As follows, the geometry is fixed supposing a geometry pipe.

$$h = \frac{Nu \cdot k}{De} \quad (3.18)$$

$$D_h = (D_o - D_{reactor}) \quad (3.19)$$

$$A_{ext} = \Pi \cdot D_h^2 \cdot L \quad (3.20)$$

$$U_0 = \frac{1}{A_o} \left( \frac{1}{\frac{1}{h_i \cdot A_i} + \frac{1}{h_o \cdot A_o} + \frac{\ln \frac{D_o}{D_i}}{2 \cdot \Pi \cdot k \cdot L} + \frac{R_{f_o}''}{A_o} + \frac{R_{f_i}''}{A_i}} \right) \quad (3.21)$$

Finally, the global heat coefficient,  $U_0$  is calculated. In table 4.1 shows the main results obtained from de design of the cooling jacket.

Table 3.1. Results obtained for the jacket and the final product in the agitator tank.

Heat exchanged	$3.24 \cdot 10^4$	Kw
Water flow	0.33	kg/s
Water input temperature	1.0	°C
Water output temperature	45.0	°C
Internal agitation tank diameter	1.0	m
External agitation tank diameter	1.3	m
Agitation tank length	1.1	m
Wet perimeter	2.23	m
<b>Cooling water</b>		
Re	$6.23 \cdot 10^6$	
Pr	2.56	
Nu	$55.22 \cdot 10^3$	
ho	83.79	W/m <sup>2</sup> K
A <sub>0</sub>	0.60	m <sup>2</sup>
<b>Final product</b>		
Re	$8.54 \cdot 10^4$	
Pr	$1.16 \cdot 10^4$	
Nu	$6.55 \cdot 10^1$	
hi	15.14	
<b>Final U<sub>0</sub></b>	$1.12 \cdot 10^3$	W/m <sup>2</sup> K

**A4. Article**

An article called “Laponite-stabilised oil-in-water emulsions viscoelasticity and thixotropy” was published in December of 2011 as the result of the study shown in chapter 5 of this report.

Cite this: *Soft Matter*, 2012, **8**, 1609

www.rsc.org/softmatter

PAPER

## Laponite-stabilised oil-in-water emulsions: viscoelasticity and thixotropy

Paula Corbi Garcia and Catherine P. Whitby\*

Received 1st September 2011, Accepted 9th November 2011

DOI: 10.1039/c1sm06660a

We have studied the breakdown and recovery of structure over time in Pickering emulsions under shear using a combination of rheology and confocal fluorescence microscopy. Oil-in-water emulsions were stabilised by laponite particles at particle and salt concentrations where the laponite dispersions form isotropic, thixotropic gels. The emulsions consist of a network of interconnected drops and particles clusters. The key result is that emulsion elasticity is sensitive to the structure of the laponite aggregates and the drop volume fraction. The stress required to break down the thixotropic laponite networks increases with the fraction of drops incorporated into the particle dispersions. At rest the network reforms, however, the presence of the drops can significantly slow recovery times.

### Introduction

Emulsions exhibit highly variable rheological behaviour that is useful in a wide range of applications, but rarely well understood. The time-dependent rheology of emulsions is important in food products, cosmetics, paints and concrete.<sup>1,2</sup> Currently, much of the interest is in using thixotropy to control the delivery (spreading, film formation, coating) of emulsions containing active ingredients.<sup>3</sup> Recently it was shown the thixotropic response of surfactant-stabilised emulsions can be controlled by loading the emulsions with clay particles.<sup>4</sup> The addition of colloidal particles confers gel-like properties which disappear on shaking, but reappear on allowing the emulsions to rest. In this work, we instead investigate the thixotropic behavior of emulsions stabilized by clay particles alone (Pickering emulsions<sup>5-7</sup>). The aim is to understand how the time-dependent rheological response of clay particle-stabilised emulsions can be controlled. In particular, the focus is to relate the macroscopic flow behavior to the emulsion microstructure.

An emulsion is defined as thixotropic if, starting from rest, its viscosity decreases with time when a constant shear is applied (breakdown).<sup>1,2</sup> When the shear ceases, the material gradually recovers its consistency and the structure it had at rest (recovery).<sup>1,2</sup> Emulsion flow behavior is determined by the competition between the spontaneous build-up of structure in the emulsion at rest and its breakdown under shear. Many emulsions show elastic and viscous behavior, depending on the time scale of the measurement. The essential difference between linear viscoelasticity and thixotropy is that the former is in the linear regime where the structure responds but remains unchanged, while the latter is a non-linear effect where the structure is broken down. Typically, the linear viscoelastic response of a rebuilding

structure, the evolution of the storage and loss moduli with time, is used as a measure of structure recovery in thixotropic materials.<sup>1,2</sup>

Thixotropy requires a microstructure that can be reversibly altered by moderate stresses, so that significant viscosity changes are induced. The changes should be relatively slow. Viscous thixotropy is observed in concentrated emulsions. Close packed drops form structure which is destroyed by deformation and restored at rest.<sup>8,9</sup> Monahan<sup>10</sup> observed that this effect can be tuned by the droplet size, with monodisperse, concentrated emulsions showing foam-like rheological behavior with appreciable thixotropy and yield stresses at drop sizes above a critical droplet radius. Thixotropy has been linked to droplet flocculation in dilute surfactant and polymer-stabilised emulsions.<sup>1</sup>

Very few studies have considered the time-dependent rheology of particle-stabilised emulsions.<sup>11-14</sup> Examination of the structure of emulsions and foams formed in the presence of clay particles revealed that significant fractions of the particles remain in the continuous phase of the emulsions.<sup>15-17</sup> These particles may impart additional stability by forming a three dimensional network with high elasticity that impedes drop coalescence. In some cases, structural changes in the particle networks have been inferred from observations of hysteresis in emulsion flow behaviour. Simon *et al.*<sup>13</sup> found that the flow behaviour of emulsions stabilized by fumed oxide particles were very similar to those of the particle dispersions, with an increase of the yield stress after emulsification and the appearance of thixotropic behavior. They deduced that the droplets strengthen the existing particle interactions in the dispersions. Identification of the length and time scales governing the mechanisms of thixotropy in Pickering emulsions remains crucial.

Laponite was chosen for this study of thixotropic particle-stabilised emulsions. It is a synthetic clay of the hectorite type, consisting of particles shaped as thin disks (or platelets) with an average diameter of 30 nm and an average thickness of 1 nm.<sup>18</sup> The particles are ionized in water, with a large number of

Ian Wark Research Institute, University of South Australia, Mawson Lakes, South Australia, 5095, Australia. E-mail: catherine.whitby@unisa.edu.au

negative charges on the faces of the disks and a few positive charges along the edges. Laponite dispersions can form thixotropic gels at particle concentrations of  $\geq 1$  wt %. Depending on the pH and ionic strength, these can occur by attractive (house of cards) or repulsive interactions.<sup>19</sup> At the moderate salt concentrations ( $\geq 10^{-3}$  M) studied, the electrostatic interactions between the particles are sufficiently screened for the anisotropy of the charge distribution around each particle to control their interactions.<sup>20</sup> Laponite particles stabilize oil-in-water emulsions under conditions where the clay particles are flocculated by the addition of salt or surfactant.<sup>15,21–23</sup>

This work examines in detail the thixotropy of materials formed by emulsifying oil droplets into laponite gels. Transient rheology was used to probe the time scales of emulsion breakdown and recovery. The length scales of the aggregate structures in the emulsions were investigated using confocal fluorescence microscopy before and after shearing. This combination of techniques shows how particle aggregation causes thixotropy in Pickering emulsions. We show a master curve is obtained for the evolution of emulsion stress with time during shearing, indicating that emulsion breakdown is determined by the flow behaviour of the laponite gel. Structure recovery is disrupted significantly, however, where the length scales of the aggregates are similar to the size of the drops incorporated into the laponite gels.

## Experimental section

### Dispersion and emulsion preparation

Laponite RD was kindly provided by Rockwood Additives Limited. Its chemical composition is: 66.2% SiO<sub>2</sub>, 30.2% MgO, 2.9% Na<sub>2</sub>O, and 0.7% Li<sub>2</sub>O, which corresponds to the chemical formula: Si<sub>8</sub>[Mg<sub>5.5</sub>Li<sub>0.4</sub>H<sub>4.0</sub>O<sub>24.0</sub>]<sup>0.7-</sup>Na<sub>0.7</sub><sup>0.7+</sup>. The density of the particles is 2.53 g cm<sup>-3</sup>.<sup>24</sup> Dispersions of the laponite in solutions of sodium chloride (Chem Supply, 99%) in water (resistivity  $\geq 18.2$  M $\Omega$  cm) were prepared using a rotor-stator mixer (Ingenieurbüro CAT X1030D, M. Zipperer GmbH) with a 19 mm head operated at 11000 revolutions per minute for 2 min to form transparent gels. The pH value of the dispersions was adjusted to 9.5 with concentrated solutions of NaOH. There is significant dissolution of magnesium silicate at pH < 7, however, dissolution is minimal at pH values above 9.<sup>25</sup> For this work, dispersions were prepared at salt and particle concentrations where thixotropic gels are obtained.

Emulsions were prepared by homogenising 1-bromohexadecane (Sigma Aldrich, 99%, passed through chromatographic alumina twice to remove polar impurities) with the aqueous laponite dispersions using the rotor-stator mixer operated at 13000 rpm. Emulsions prepared at oil volume fractions,  $\phi_o \leq 0.4$  and laponite concentrations in the aqueous phase,  $C_p > 1.0$  wt.% did not coalesce for several weeks. During this period the mean and polydispersity (taken as the ratio of the standard deviation to the mean) of the droplet size distributions obtained from microscope images of the emulsions (discussed shortly) varied by <7%. Dilution of the emulsions in pure water (rather than a laponite dispersion) did not cause immediate droplet coalescence, confirming that Pickering emulsions had been prepared. Care was also taken to ensure that the gel strength was sufficient to hinder drop creaming for several weeks. Emulsions were

diluted in laponite dispersions (at the same salt concentration) to achieve the required volume fraction for rheology measurements. The dispersions and emulsions were stored in screw-cap vials at 25 °C.

### Dispersion and emulsion rheology

Rheological measurements were made using a Rheometric Scientific Dynamic Stress Rheometer SR2000 in the controlled rate mode with a cone and plate geometry at a fixed temperature of  $25 \pm 0.1$  °C. Geometries with either smooth hydrophobic surfaces or roughened (by sand blasting) steel surfaces were used to minimise wall slip effects. A solvent trap was used to prevent evaporation. Samples were typically stirred by hand for 30 s, loaded into the rheometer and then left to rest for 180 s prior to measurements. Initial measurements confirmed that reproducible results were obtained using this pre-shearing method.

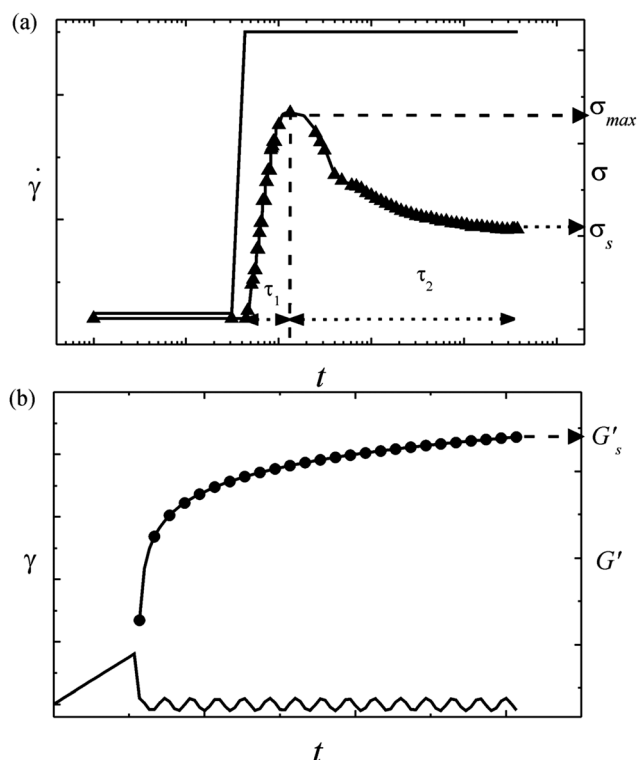
For oscillatory measurements, viscoelastic moduli were measured as the strain of the oscillation was scanned in a series of logarithmic steps at a constant frequency. The lowest strain applied was the lowest achievable by the rheometer, while the upper strain was below that at which the emulsions were ejected. After a fresh sample was preconditioned, the frequency of the oscillation was then scanned from a higher to a lower limit at a constant stress chosen from the stress range where the maximum stress response was low and a linear function of the maximum applied strain.

The thixotropic behavior of the dispersions and emulsions was characterized using the methods shown schematically in Fig. 1. These are based on established procedures for studying the time-dependent rheology of gelled dispersions. Breakdown tests involved measuring the stress response while applying a jump in the shear rate from an initial value (typically  $0$  s<sup>-1</sup>) to a final value (typically  $5$  s<sup>-1</sup>). Recovery tests involved applying a fixed small sinusoidal strain (corresponding to the linear viscoelastic region) after breakdown. The change in the viscoelastic moduli over time was measured.

### Confocal fluorescence microscopy

Confocal fluorescence microscopy (CFM, Leica SP5 spectra scanning confocal microscope) was used to visualise both dispersions and emulsions containing Rhodamine B (Sigma, 97%). At the low concentration used ( $\sim 0.3$   $\mu$ M) the dye adsorbs completely onto the laponite particles. The samples were excited at a wavelength of 514 nm and the fluorescence emission intensity collected over 555 to 655 nm. The particles appeared bright, while the aqueous and oil phases were black (images shown later). The mean droplet size was calculated from at least 50 individual measurements of drop diameters in the confocal images.

The particle aggregate structure was characterized using the image analysis software, Image J. Micrographs (512 pixels  $\times$  512 pixels) were converted into 8-bit grayscale images. The mean of the grey level histogram was used as the threshold level for creating binary images. The pores in the structures were counted and the size of the pores,  $A_p$ , calculated from the number of pixels in each pore (the area of a pixel was  $\sim 0.04$   $\mu$ m<sup>2</sup>). The fractal character of the particle networks in the particle dispersions was



**Fig. 1** Procedures used to characterize emulsion thixotropic behavior. (a) The emulsion breakdown was tested by stepping up (or down) the shear rate ( $\dot{\gamma}$ , —). The transient emulsion stress ( $\sigma$ , —▲—) passes through a maximum ( $\sigma_{max}$ ) before reaching steady flow conditions ( $\sigma_f$ ). The times scales of the breakdown and relaxation periods are denoted by  $\tau_1$  and  $\tau_2$ , respectively. (b) After shearing the emulsion recovery is monitored by applying a weak oscillatory strain ( $\gamma$ , —●—) and measuring the evolution of elastic storage modulus ( $G'$ , —●—).

analysed by the box counting method. In this method, grids of decreasing size are placed over an image and the number of boxes containing pixels (due to particle aggregates) is counted for each box size. The fractal dimension is given by

$$D_f = -\lim_{\epsilon \rightarrow 0} \frac{\ln N_\epsilon}{\ln \epsilon} \quad (1)$$

where  $N_\epsilon$ , the number of boxes of size  $\epsilon$  containing pixels. The box size,  $\epsilon$ , is given by the ratio of the box area to the total image area. For each  $\epsilon$ , the coefficient of variation in the pixel distribution,  $A_\epsilon$ , is calculated using

$$A_\epsilon = \left( \frac{\sigma_\epsilon}{\mu} \right)^2 \quad (2)$$

where  $\sigma_\epsilon$  is the standard deviation and  $\mu$  is the average number of pixels per box for the same grid size. The lacunarity,  $L$ , is the mean value of  $A_\epsilon$  over all  $\epsilon$ . The size of the boxes used was varied to identify the cut-off distance ( $L_c$ ) above which, the structure becomes homogenous and the fractal scaling disappears ( $D_f = 2$ ).

## Results and discussion

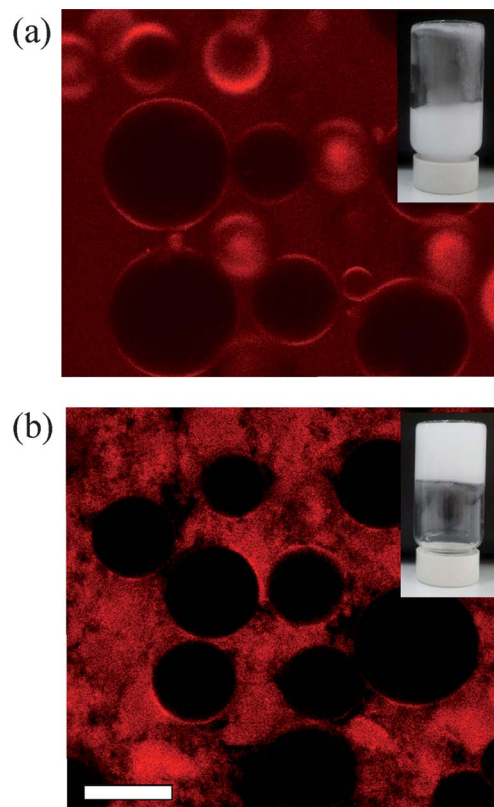
Coagulation of the laponite particles leads to complex structures in the emulsions as the interactions between the particles cause

rapid growth of large particle clusters. The oil droplets are trapped within these super-aggregate particulate structures. The resulting structure is a network of interconnected drops and particles that spans the whole emulsion volume, as shown in Fig. 2. The aggregate size varies with the salt concentration in the aqueous phase (Fig. 2). This super-aggregate structure has a critical influence on the emulsion breakdown and recovery behavior. The emulsions are solid-like materials which exhibit enhanced viscosity and yield stress compared to laponite dispersions alone. The dynamic rheological behaviour of the dispersions and emulsions in the linear viscoelastic regime was used to characterize the dispersions and emulsions at rest.

### Gelled laponite dispersion characterisation

Rheology measurements were initially made at different times after preparation of the laponite dispersions, to investigate the aging kinetics of the dispersions. The viscous flow and oscillatory response are reproducible after about 24 h, indicating that the fast aging processes in the dispersions were completed. Slower aging processes occur over a time period of several weeks.<sup>26</sup> All the results shown here were obtained within 72 h of preparation avoid any effect of the slow aging dynamics of the laponite dispersions.

The gelled laponite dispersions used to stabilise the emulsions exhibit a yield stress ( $\sigma_y$ ) and an elastic storage modulus,  $G'$ , which is much higher than their viscous loss modulus,  $G''$ .  $G'$



**Fig. 2** Confocal fluorescence images of the structure in 20 vol% bromohexadecane-in-water emulsions stabilized by 2 wt% particles at (a) 0.002 M and (b) 0.01 M NaCl. The scale bar corresponds to 50  $\mu\text{m}$ . Inset in each image is a photo of the emulsion in an inverted sample tube.

shows limited dependence on the frequency of the oscillatory stress being applied. The average value of  $G'$  increases with the particle concentration, as shown in Fig. 3. The particle concentration is plotted relative to the concentration at which gelation occurs for a given salt concentration.<sup>27</sup> The elasticity data scale with the reduced particle concentration as

$$G' = A(C_p - C_0)^\alpha \quad (3)$$

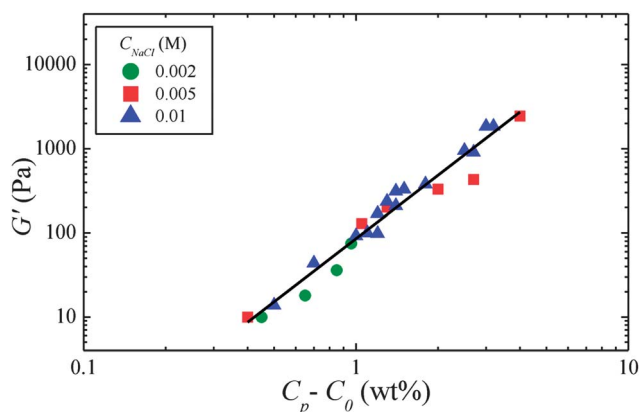
The scaling exponent ( $\alpha = 2.5$ ) does not depend on the clay or salt concentration. It is close to the exponents measured in earlier studies of laponite and of other clays, including nontronite and montmorillonite.<sup>28</sup> This power appears to be characteristic of all swelling clays.

Analysis of the dispersion yield stress values shows that they also fall on a master curve when plotted as a function of the reduced particle concentration ( $C_p - C_0$ ). The yield stress values are systematically lower than the elasticity values. The yield stress is a linear function of the elasticity as given by

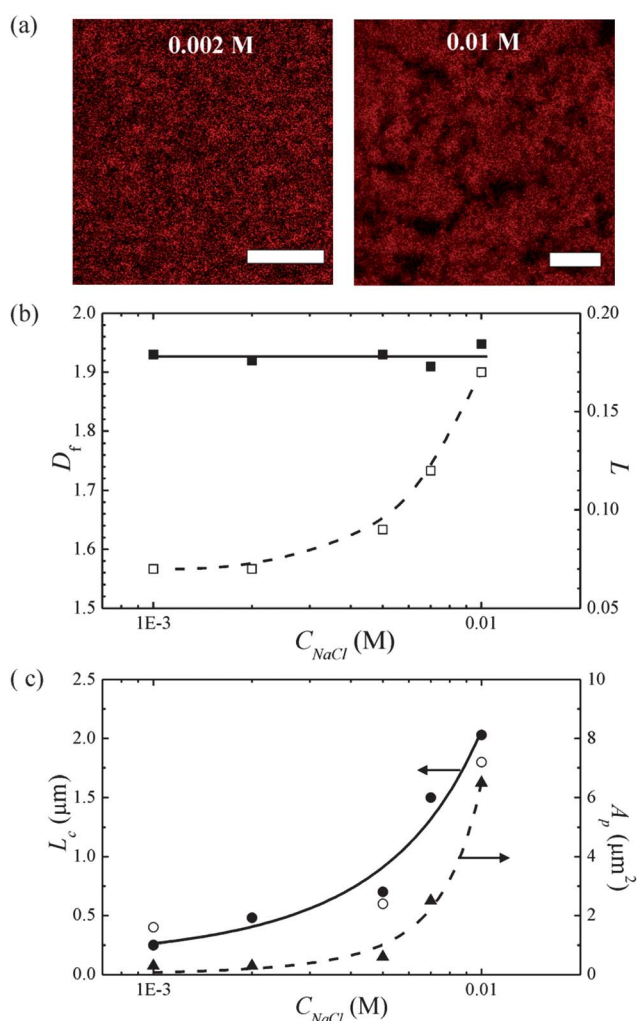
$$\sigma_y = G' \gamma_c \quad (4)$$

where  $\gamma_c$  is the critical strain of the dispersions.  $\gamma_c$  is typically about 0.1 for these laponite dispersions. Similar relationships have been observed between the yield stress and elasticity of other anisometric particles (nontronites, montmorillonites, hectorites, beidellites).<sup>28</sup>

The internal structure of the laponite gels was observed using confocal fluorescence microscopy. The laponite particles were stained with Rhodamine B. Heterogeneous structures with zones of denser and less dense particle aggregates are observed in images of laponite dispersions prepared at different salt concentrations, as shown in Fig. 4a. At rest, laponite particles aggregate into micrometre-sized domains. The loose connection of these micrometre-sized aggregates gives the continuous, three dimensional structures observed in the confocal images (Fig. 4a). The structures have a fractal dimension  $D_f \sim 1.9$  (Fig. 4b). These observations are consistent with the characteristic length scales



**Fig. 3** Particle concentration ( $C_p$ ) dependence of the laponite dispersion elastic modulus ( $G'$ ). The particle concentration is reduced by  $C_0$ , the solid fraction above which a viscoelastic gel appears. The salt concentration in the dispersions ( $C_{NaCl}$ ) is shown in the legend. The solid line corresponds to eqn (3) with  $\alpha = 2.5$ .



**Fig. 4** (a) Confocal fluorescence images of floc structure in 2 wt% laponite dispersions at the salt concentrations shown on the images. The scale bars correspond to 10  $\mu\text{m}$ . (b) Salt concentration ( $C_{NaCl}$ ) dependence of the fractal dimension ( $D_f$ ,  $\blacksquare$ ) and lacunarity ( $L$ ,  $\square$ ) of the coagulated particle networks formed the laponite dispersions. Lines are shown to guide the eye. (c) Salt concentration dependence of the maximum cut-off distance ( $L_c$ ,  $\bullet$ ,  $\circ$ ) and average pore area ( $A_p$ ,  $\blacktriangle$ ) of the coagulated particle networks formed in dispersions (filled symbols) and emulsions (open symbols). Lines are shown to guide the eye.

and fractal behavior deduced from neutron and light scattering studies of laponite dispersions.<sup>20</sup>

Although the fractal dimension remains the same, the particle network seems less homogeneous at higher salt concentrations. As the salt concentration increases, the rate of particle aggregation increases (shown later). The fractal character of the network is observed up to longer length scales, as shown by the increase in the upper spatial cut-off limit ( $L_c$ ) for the fractal scaling with the salt concentration (Fig. 4c). The size of the pores in the aggregates increases with the salt concentration (Fig. 4c). Another contributing factor is the coarser aggregate structures at higher salt concentrations which results in more variation in the pore shapes. Overall, these changes in the microstructure can be characterized by the lacunarity, which is a measure of the structural heterogeneity.<sup>29</sup> Lacunarity is used as a complementary

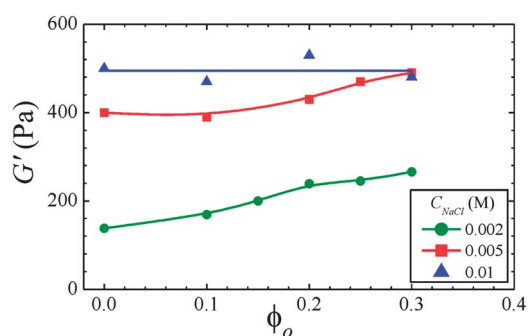
measurement to the fractal dimension.  $L$  is a measure of the variability in the pixel counts about the average values used in the standard box counting procedure to estimate  $D_f$ . Fig. 4b shows that the lacunarity increases with salt concentration as larger pores are incorporated into the particle networks.

### Laponite-stabilised emulsion characterisation

Emulsification times were set to obtain roughly similar drop size distributions (number average radius  $\sim 20 \mu\text{m}$ ) in the emulsions studied. The emulsions were diluted at constant particle and salt concentration to investigate the effect of oil volume fraction on the emulsion elasticity. The mechanical state of the laponite dispersions used to stabilise the emulsions was fixed by adjusting the laponite concentration relative to that required for gelation. This parameter depends only on the salt concentration in the dispersion. Typically the particle concentration was chosen to be close to that required for gelation. The maximum length scale at which the fractal character of the particle networks in the continuous phase of the emulsions was observed are similar to the spatial cut-off limits in the particle dispersions (Fig. 4c).

The elasticity values obtained for emulsions stabilized by 2wt% gelled laponite dispersions are summarized in Fig. 5a. The oil volume fraction dependence of the emulsion elasticity varies significantly with the salt concentration. At salt concentrations just above that required to cause gelation of the dispersions the emulsion elasticity increases with the drop volume fraction. At higher salt concentrations, the rheological behavior of the emulsions is dominated by the behavior of the coagulated laponite dispersions. There is less variation in  $G'$  with  $\phi_o$  at the oil volume fractions studied.

The emulsions show significant elasticity at drop volume fractions well below that required for close packing of the drops ( $\phi_m \sim 0.64$ ) due to the presence of the aggregated laponite particles in the emulsion continuous phase. Effectively, the emulsions behave as suspensions of large oil drops embedded in a gelled suspension of clay particles. Since the emulsion rheology is determined primarily by the flow behavior of the laponite dispersions, the emulsions can be treated as filled polymer gels. Assuming that the effective elastic modulus of the drops is larger than that of the laponite gel, then the reinforcement of the laponite gel strength by the drops will be a function of the drop volume fraction and the ratio of the droplet and dispersion

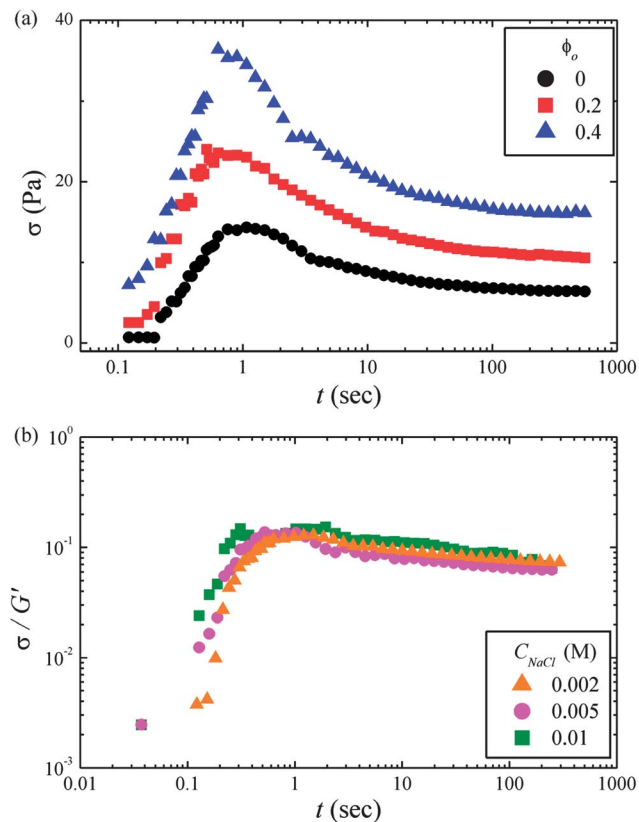


**Fig. 5** Volume fraction ( $\phi_o$ ) dependence of the elastic storage modulus ( $G'$ ) of emulsions stabilized by 2 wt% particles at different salt concentrations.

moduli.<sup>30</sup> Thus the influence of the oil droplets on the emulsion rheology decreases as the gel strength of the laponite dispersions increases (Fig. 5a). The kinetics of structure formation in the dispersions is relatively slow at low salt concentrations (shown later). It is possible that this enables greater incorporation of laponite particles attached to the drop surfaces into the super-aggregate structures formed by the laponite particles in the continuous phase of the emulsions. So the drops also are more efficient at enhancing the gel strength of laponite dispersions at lower salt concentrations. Dickinson and Chen<sup>30</sup> observed similar variations in the rheology of protein-stabilised emulsion gels with the protein gel strength.

### Emulsion thixotropy

The thixotropic behaviour of the emulsions is illustrated by two kinds of results: destruction of the network by shear and recovery after cessation of the shear. Fig. 6a shows the transient response of the emulsions when a constant shear rate is applied. The emulsions follow a curve that is characteristic of the dispersions used to stabilize the emulsions. At short times the stress increases linearly with time indicating that the emulsion deformation is elastic. The maximum stress reached is related to the yield stress of the emulsion. Beyond this maximum, the emulsions start to



**Fig. 6** (a) Time ( $t$ ) dependence of the shear stress ( $\sigma$ ) of emulsions at different oil volume fractions being sheared at a rate of  $5 \text{ s}^{-1}$ .  $C_p = 2 \text{ wt}\%$ ,  $C_{\text{NaCl}} = 0.002 \text{ M}$  NaCl. (b) Time dependence of the emulsion shear stress scaled by the elastic storage modulus ( $G'$ ) for emulsions prepared at different salt concentrations.  $\phi_o = 0.2$ ,  $C_p = 2 \text{ wt}\%$ .

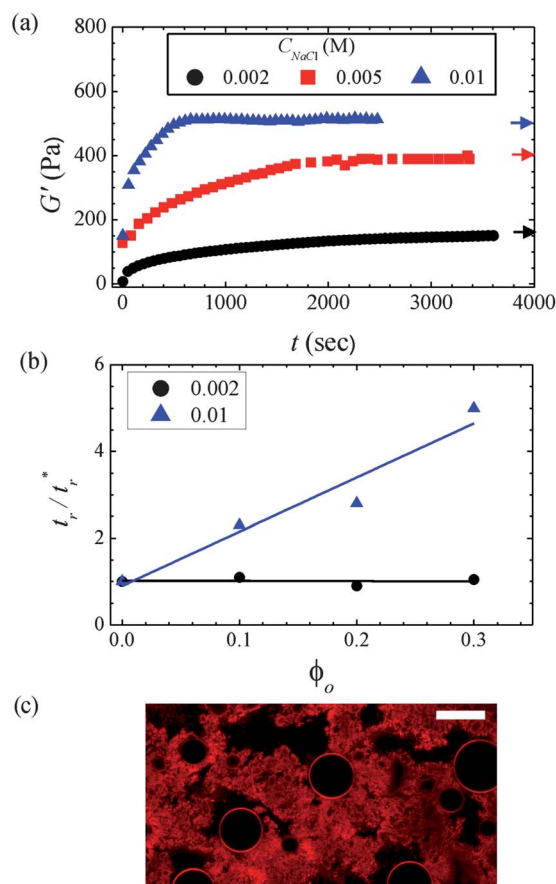
flow and the stress relaxes until a steady flow regime is reached. The decrease corresponds to breakdown of the network.<sup>31</sup>

The time-dependent changes in stress reveal two periods with distinct time scales in the breakdown process, situated on either side of the maximum stress and corresponding critical strain. The first period corresponds to elastic strain of the material and orientation of the structure. The second corresponds to flow and disaggregation of the structure. The order of magnitude of the time scale in the first period is shorter than that in the second. The relaxation behavior of the emulsions is slow, consistent with the presence of large scale structure formation in the emulsions observed in the confocal microscope images (Fig. 2). The first period lasts for about 1 s and the second up to 1000 s, giving a time scale ratio of 1/1000. The influence of shear rate on the characteristic times of breakdown was investigated by measuring the time-dependent changes in stress for various shear rates. The kinetics of breakdown differs depending on the shear rate applied, however, the ratio of the time scales remains about the same.

The maximum stress and the steady state stress reached when a constant shear rate is applied increase with the drop volume fraction in the emulsions. This occurs in particular for emulsions prepared at low salt concentrations, where the drops are more readily incorporated into the laponite super-aggregate structures. It is possible, however, to draw a master curve for these different relaxation curves by scaling the stress by the elastic storage modulus of the emulsion, as shown in Fig. 6b. Furthermore, all stress relaxation data for emulsions prepared at the same drop size could be normalized in this way (Fig. 6b). This means that the relaxation behaviour of laponite-stabilised emulsions is determined primarily by that of the dispersions used to stabilize the emulsions.

After breakdown measurements, the emulsions were subjected to a low-strain harmonic shearing so the kinetics of recovery could be monitored. The levels reached for  $G'$  (and  $G''$ ) increase with the salt concentration, as shown in Fig. 7a. The evolution in  $G'$  with time followed similar trends to that observed for the particle dispersions alone. Typically there are two periods in the recovery curves. The first period lasts up to a few minutes and the rate of increase in  $G'$  is several times faster than the second period, which takes up to 30 min. For a given emulsion, the maximum elasticity reached is consistent with the value measured in a dynamic oscillatory test.

The recovery of the emulsion elasticity is increasingly rapid as the salt concentration or the particle concentration increases. In particular, the kinetics of the increase in  $G'$  in the second period increase and hence the total time ( $t_r$ ) required to reach the final  $G'$  value decreases with increasing salt concentration, as shown in Fig. 7a. This is consistent with the large scale particle networks observed in the continuous phase of emulsions at high salt concentrations (Fig. 2). Importantly, incorporation of oil drops into highly elastic laponite dispersions can cause significant changes to the recovery behaviour. The recovery time can increase substantially as the drop volume fraction increases, as shown in Fig. 7b. This implies that recovery of the fractal character of the large scale structures (which are up to tens of micrometres in length) in the continuous phase of the emulsions prepared at high salt concentrations is hindered by the presence of drops (40  $\mu\text{m}$  in diameter). Examination of the structure in confocal fluorescence microscope images of these emulsions



**Fig. 7** (a) Time dependence of the elastic storage modulus ( $G'$ ) of emulsions at different salt concentrations after being sheared at a rate of  $50 \text{ s}^{-1}$  for 2 min. The arrows indicate the value of  $G'$  measured prior to shearing.  $C_p = 2 \text{ wt}\%$ ,  $\phi_o = 0.1$ . (b) Drop volume fraction dependence of the time taken to reach steady  $G'$  values ( $t_r$ ) for emulsions after shearing at a rate of  $10 \text{ s}^{-1}$ . The recovery time is scaled by that of the particle dispersion.  $C_p = 2 \text{ wt}\%$ . (c) Confocal fluorescence image of the structure in an emulsion at  $0.01 \text{ M NaCl}$  after shearing.

revealed that shearing disrupts the particle network structures, as shown in Fig. 7c. The extent of the network disruption increases with increasing strain on the emulsion during the breakdown period. This presumably produces a relatively homogeneous broken-down structure which can aggregate rather quickly. Thus recovery times tend to decrease as the shearing rate applied during breakdown increases. In contrast, recovery times for emulsions prepared at lower salt concentrations do not vary substantially with the drop volume fraction (Fig. 7b). Presumably, the smaller sized aggregate structures that form in these emulsions are more easily disrupted. Future experiments will investigate the role of the interactions between the droplet surfaces with the laponite network structures on structure recovery in the emulsions.

## Conclusions

Thixotropic emulsions were formed by stabilizing emulsions with laponite particles alone. They are hierarchically organized and consist of oil drops stabilized by laponite particles attached to their surfaces and incorporated into a three dimensional network

structure of particles. The laponite particles coagulate in the aqueous phase into dense microdomains that are connected into super-aggregates. The rate of aggregation and hence size of the aggregates is determined primarily by the salt concentration. The transient flow behavior of the emulsions reflects the complex structure of these systems. The mechanical properties of the emulsions depend on the mechanical properties of the laponite dispersions and the oil drop volume fraction.

## Acknowledgements

The particles were kindly supplied by Rockwood Additives Limited. We thank L. Waterhouse (Adelaide Microscopy, The University of Adelaide) for help with the confocal fluorescence microscopy experiments. CPW acknowledges receipt of an Australian Research Council Future Fellowship.

## References

- 1 H. A. Barnes, *J. Non-Newtonian Fluid Mech.*, 1997, **70**, 1.
- 2 J. Mewis and N. J. Wagner, *Adv. Colloid Interface Sci.*, 2009, **147–148**, 214.
- 3 C. H. Lee, V. Moturi and Y. Lee, *J. Controlled Release*, 2009, **136**, 88.
- 4 A. Ragouilliaux, G. Ovarlez, N. Shahidzadeh-Bonn, B. Herzhaft, T. Palermo and P. Coussot, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2007, **76**, 051408.
- 5 B. P. Binks, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 21.
- 6 E. Dickinson, *Curr. Opin. Colloid Interface Sci.*, 2010, **15**, 40.
- 7 F. Leal-Calderon and V. Schmitt, *Curr. Opin. Colloid Interface Sci.*, 2008, **13**, 217.
- 8 P. Coussot, H. Tabuteau, X. Chateau, L. Tocquer and G. Ovarlez, *J. Rheol.*, 2006, **50**, 975.
- 9 A. Fall, J. Paredes and D. Bonn, *Phys. Rev. Lett.*, 2010, **105**, 225502.
- 10 N. Monahan, Thesis, Victoria University of Wellington, 2010.
- 11 S. Abend, N. Bonnke, U. Gutschner and G. Lagaly, *Colloid Polym. Sci.*, 1998, **276**, 730.
- 12 J. Chen, R. Vogel, S. Werner, G. Heinrich, D. Clause and V. Dutschk, *Colloids Surf., A*, 2011, **382**, 238.
- 13 S. Simon, S. Theiler, A. Knudsen, G. Oye and J. Sjoblom, *J. Dispersion Sci. Technol.*, 2010, **31**, 632.
- 14 N. Sugita, S. Nomura and M. Kawaguchi, *J. Dispersion Sci. Technol.*, 2008, **29**, 931.
- 15 Y. Cui, M. Threlfall and J. S. van Duijneveldt, *J. Colloid Interface Sci.*, 2011, **356**, 665.
- 16 J. Thieme, S. Abend and G. Lagaly, *Colloid Polym. Sci.*, 1999, **277**, 257.
- 17 S. Zhang, D. Sun, X. Dong, C. Li and J. Xu, *Colloids Surf., A*, 2008, **324**, 1.
- 18 R. G. Avery and J. D. F. Ramsay, *J. Colloid Interface Sci.*, 1986, **109**, 448.
- 19 J. M. Saunders, J. W. Goodwin, R. M. Richardson and B. J. Vincent, *J. Phys. Chem. B*, 1999, **103**, 9211.
- 20 F. Pignon, A. Magnin, J. M. Piau, B. Cabane, P. Lindner and O. Diat, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 1997, **56**, 3281.
- 21 S. A. F. Bon and P. J. Colver, *Langmuir*, 2007, **23**, 8316.
- 22 S. Guillot, F. Bergaya, C. de Azevedo, F. Warmont and J.-F. Tranchant, *J. Colloid Interface Sci.*, 2009, **333**, 563.
- 23 J. Wang, G. Liu, L. Wang, C. Li, J. Xu and D. Sun, *Colloids Surf., A*, 2010, **353**, 117.
- 24 L. Rosta and H. R. Vongunten, *J. Colloid Interface Sci.*, 1990, **134**, 397.
- 25 D. W. Thompson and J. T. Butterworth, *J. Colloid Interface Sci.*, 1992, **151**, 236.
- 26 S. Bhatia, J. Barker and A. Mourchid, *Langmuir*, 2003, **19**, 532.
- 27 A. Mourchid, E. Lecolier, H. Van Damme and P. Levitz, *Langmuir*, 1998, **14**, 4718.
- 28 E. Paineau, L. J. Michot, I. Bihannic and C. Baravian, *Langmuir*, 2011, **27**, 7806.
- 29 T. G. Smith, G. D. Lange and W. B. Marks, *J. Neurosci. Methods*, 1996, **69**, 123.
- 30 E. Dickinson and J. S. Chen, *J. Dispersion Sci. Technol.*, 1999, **20**, 197.
- 31 F. Pignon, A. Magnin and J. M. Piau, *J. Rheol.*, 1998, **42**, 1349.

Cite this: *Soft Matter*, 2012, **8**, 1609

www.rsc.org/softmatter

PAPER

## Laponite-stabilised oil-in-water emulsions: viscoelasticity and thixotropy

Paula Corbi Garcia and Catherine P. Whitby\*

Received 1st September 2011, Accepted 9th November 2011

DOI: 10.1039/c1sm06660a

We have studied the breakdown and recovery of structure over time in Pickering emulsions under shear using a combination of rheology and confocal fluorescence microscopy. Oil-in-water emulsions were stabilised by laponite particles at particle and salt concentrations where the laponite dispersions form isotropic, thixotropic gels. The emulsions consist of a network of interconnected drops and particles clusters. The key result is that emulsion elasticity is sensitive to the structure of the laponite aggregates and the drop volume fraction. The stress required to break down the thixotropic laponite networks increases with the fraction of drops incorporated into the particle dispersions. At rest the network reforms, however, the presence of the drops can significantly slow recovery times.

### Introduction

Emulsions exhibit highly variable rheological behaviour that is useful in a wide range of applications, but rarely well understood. The time-dependent rheology of emulsions is important in food products, cosmetics, paints and concrete.<sup>1,2</sup> Currently, much of the interest is in using thixotropy to control the delivery (spreading, film formation, coating) of emulsions containing active ingredients.<sup>3</sup> Recently it was shown the thixotropic response of surfactant-stabilised emulsions can be controlled by loading the emulsions with clay particles.<sup>4</sup> The addition of colloidal particles confers gel-like properties which disappear on shaking, but reappear on allowing the emulsions to rest. In this work, we instead investigate the thixotropic behavior of emulsions stabilized by clay particles alone (Pickering emulsions<sup>5-7</sup>). The aim is to understand how the time-dependent rheological response of clay particle-stabilised emulsions can be controlled. In particular, the focus is to relate the macroscopic flow behavior to the emulsion microstructure.

An emulsion is defined as thixotropic if, starting from rest, its viscosity decreases with time when a constant shear is applied (breakdown).<sup>1,2</sup> When the shear ceases, the material gradually recovers its consistency and the structure it had at rest (recovery).<sup>1,2</sup> Emulsion flow behavior is determined by the competition between the spontaneous build-up of structure in the emulsion at rest and its breakdown under shear. Many emulsions show elastic and viscous behavior, depending on the time scale of the measurement. The essential difference between linear viscoelasticity and thixotropy is that the former is in the linear regime where the structure responds but remains unchanged, while the latter is a non-linear effect where the structure is broken down. Typically, the linear viscoelastic response of a rebuilding

structure, the evolution of the storage and loss moduli with time, is used as a measure of structure recovery in thixotropic materials.<sup>1,2</sup>

Thixotropy requires a microstructure that can be reversibly altered by moderate stresses, so that significant viscosity changes are induced. The changes should be relatively slow. Viscous thixotropy is observed in concentrated emulsions. Close packed drops form structure which is destroyed by deformation and restored at rest.<sup>8,9</sup> Monahan<sup>10</sup> observed that this effect can be tuned by the droplet size, with monodisperse, concentrated emulsions showing foam-like rheological behavior with appreciable thixotropy and yield stresses at drop sizes above a critical droplet radius. Thixotropy has been linked to droplet flocculation in dilute surfactant and polymer-stabilised emulsions.<sup>1</sup>

Very few studies have considered the time-dependent rheology of particle-stabilised emulsions.<sup>11-14</sup> Examination of the structure of emulsions and foams formed in the presence of clay particles revealed that significant fractions of the particles remain in the continuous phase of the emulsions.<sup>15-17</sup> These particles may impart additional stability by forming a three dimensional network with high elasticity that impedes drop coalescence. In some cases, structural changes in the particle networks have been inferred from observations of hysteresis in emulsion flow behaviour. Simon *et al.*<sup>13</sup> found that the flow behaviour of emulsions stabilized by fumed oxide particles were very similar to those of the particle dispersions, with an increase of the yield stress after emulsification and the appearance of thixotropic behavior. They deduced that the droplets strengthen the existing particle interactions in the dispersions. Identification of the length and time scales governing the mechanisms of thixotropy in Pickering emulsions remains crucial.

Laponite was chosen for this study of thixotropic particle-stabilised emulsions. It is a synthetic clay of the hectorite type, consisting of particles shaped as thin disks (or platelets) with an average diameter of 30 nm and an average thickness of 1 nm.<sup>18</sup> The particles are ionized in water, with a large number of

Ian Wark Research Institute, University of South Australia, Mawson Lakes, South Australia, 5095, Australia. E-mail: catherine.whitby@unisa.edu.au

negative charges on the faces of the disks and a few positive charges along the edges. Laponite dispersions can form thixotropic gels at particle concentrations of  $\geq 1$  wt %. Depending on the pH and ionic strength, these can occur by attractive (house of cards) or repulsive interactions.<sup>19</sup> At the moderate salt concentrations ( $\geq 10^{-3}$  M) studied, the electrostatic interactions between the particles are sufficiently screened for the anisotropy of the charge distribution around each particle to control their interactions.<sup>20</sup> Laponite particles stabilize oil-in-water emulsions under conditions where the clay particles are flocculated by the addition of salt or surfactant.<sup>15,21–23</sup>

This work examines in detail the thixotropy of materials formed by emulsifying oil droplets into laponite gels. Transient rheology was used to probe the time scales of emulsion breakdown and recovery. The length scales of the aggregate structures in the emulsions were investigated using confocal fluorescence microscopy before and after shearing. This combination of techniques shows how particle aggregation causes thixotropy in Pickering emulsions. We show a master curve is obtained for the evolution of emulsion stress with time during shearing, indicating that emulsion breakdown is determined by the flow behaviour of the laponite gel. Structure recovery is disrupted significantly, however, where the length scales of the aggregates are similar to the size of the drops incorporated into the laponite gels.

## Experimental section

### Dispersion and emulsion preparation

Laponite RD was kindly provided by Rockwood Additives Limited. Its chemical composition is: 66.2% SiO<sub>2</sub>, 30.2% MgO, 2.9% Na<sub>2</sub>O, and 0.7% Li<sub>2</sub>O, which corresponds to the chemical formula: Si<sub>8</sub>[Mg<sub>5.5</sub>Li<sub>0.4</sub>H<sub>4.0</sub>O<sub>24.0</sub>]<sup>0.7-</sup>Na<sub>0.7</sub><sup>0.7+</sup>. The density of the particles is 2.53 g cm<sup>-3</sup>.<sup>24</sup> Dispersions of the laponite in solutions of sodium chloride (Chem Supply, 99%) in water (resistivity  $\geq 18.2$  M $\Omega$  cm) were prepared using a rotor-stator mixer (Ingenieurbüro CAT X1030D, M. Zipperer GmbH) with a 19 mm head operated at 11000 revolutions per minute for 2 min to form transparent gels. The pH value of the dispersions was adjusted to 9.5 with concentrated solutions of NaOH. There is significant dissolution of magnesium silicate at pH < 7, however, dissolution is minimal at pH values above 9.<sup>25</sup> For this work, dispersions were prepared at salt and particle concentrations where thixotropic gels are obtained.

Emulsions were prepared by homogenising 1-bromohexadecane (Sigma Aldrich, 99%, passed through chromatographic alumina twice to remove polar impurities) with the aqueous laponite dispersions using the rotor-stator mixer operated at 13000 rpm. Emulsions prepared at oil volume fractions,  $\phi_o \leq 0.4$  and laponite concentrations in the aqueous phase,  $C_p > 1.0$  wt.% did not coalesce for several weeks. During this period the mean and polydispersity (taken as the ratio of the standard deviation to the mean) of the droplet size distributions obtained from microscope images of the emulsions (discussed shortly) varied by <7%. Dilution of the emulsions in pure water (rather than a laponite dispersion) did not cause immediate droplet coalescence, confirming that Pickering emulsions had been prepared. Care was also taken to ensure that the gel strength was sufficient to hinder drop creaming for several weeks. Emulsions were

diluted in laponite dispersions (at the same salt concentration) to achieve the required volume fraction for rheology measurements. The dispersions and emulsions were stored in screw-cap vials at 25 °C.

### Dispersion and emulsion rheology

Rheological measurements were made using a Rheometric Scientific Dynamic Stress Rheometer SR2000 in the controlled rate mode with a cone and plate geometry at a fixed temperature of  $25 \pm 0.1$  °C. Geometries with either smooth hydrophobic surfaces or roughened (by sand blasting) steel surfaces were used to minimise wall slip effects. A solvent trap was used to prevent evaporation. Samples were typically stirred by hand for 30 s, loaded into the rheometer and then left to rest for 180 s prior to measurements. Initial measurements confirmed that reproducible results were obtained using this pre-shearing method.

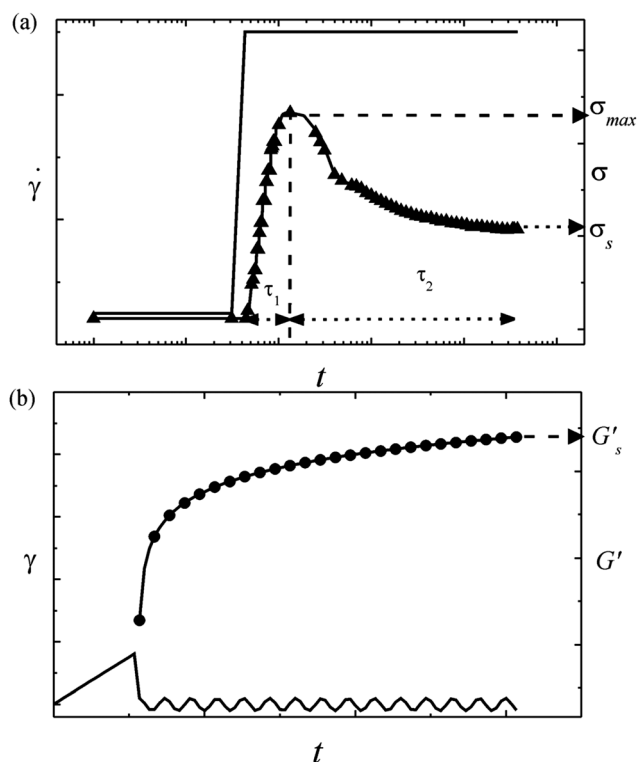
For oscillatory measurements, viscoelastic moduli were measured as the strain of the oscillation was scanned in a series of logarithmic steps at a constant frequency. The lowest strain applied was the lowest achievable by the rheometer, while the upper strain was below that at which the emulsions were ejected. After a fresh sample was preconditioned, the frequency of the oscillation was then scanned from a higher to a lower limit at a constant stress chosen from the stress range where the maximum stress response was low and a linear function of the maximum applied strain.

The thixotropic behavior of the dispersions and emulsions was characterized using the methods shown schematically in Fig. 1. These are based on established procedures for studying the time-dependent rheology of gelled dispersions. Breakdown tests involved measuring the stress response while applying a jump in the shear rate from an initial value (typically  $0$  s<sup>-1</sup>) to a final value (typically  $5$  s<sup>-1</sup>). Recovery tests involved applying a fixed small sinusoidal strain (corresponding to the linear viscoelastic region) after breakdown. The change in the viscoelastic moduli over time was measured.

### Confocal fluorescence microscopy

Confocal fluorescence microscopy (CFM, Leica SP5 spectra scanning confocal microscope) was used to visualise both dispersions and emulsions containing Rhodamine B (Sigma, 97%). At the low concentration used ( $\sim 0.3$   $\mu$ M) the dye adsorbs completely onto the laponite particles. The samples were excited at a wavelength of 514 nm and the fluorescence emission intensity collected over 555 to 655 nm. The particles appeared bright, while the aqueous and oil phases were black (images shown later). The mean droplet size was calculated from at least 50 individual measurements of drop diameters in the confocal images.

The particle aggregate structure was characterized using the image analysis software, Image J. Micrographs (512 pixels  $\times$  512 pixels) were converted into 8-bit grayscale images. The mean of the grey level histogram was used as the threshold level for creating binary images. The pores in the structures were counted and the size of the pores,  $A_p$ , calculated from the number of pixels in each pore (the area of a pixel was  $\sim 0.04$   $\mu$ m<sup>2</sup>). The fractal character of the particle networks in the particle dispersions was



**Fig. 1** Procedures used to characterize emulsion thixotropic behavior. (a) The emulsion breakdown was tested by stepping up (or down) the shear rate ( $\dot{\gamma}$ , —). The transient emulsion stress ( $\sigma$ , —▲—) passes through a maximum ( $\sigma_{max}$ ) before reaching steady flow conditions ( $\sigma_s$ ). The times scales of the breakdown and relaxation periods are denoted by  $\tau_1$  and  $\tau_2$ , respectively. (b) After shearing the emulsion recovery is monitored by applying a weak oscillatory strain ( $\gamma$ , —●—) and measuring the evolution of elastic storage modulus ( $G'$ , —●—).

analysed by the box counting method. In this method, grids of decreasing size are placed over an image and the number of boxes containing pixels (due to particle aggregates) is counted for each box size. The fractal dimension is given by

$$D_f = -\lim_{\epsilon \rightarrow 0} \frac{\ln N_\epsilon}{\ln \epsilon} \quad (1)$$

where  $N_\epsilon$ , the number of boxes of size  $\epsilon$  containing pixels. The box size,  $\epsilon$ , is given by the ratio of the box area to the total image area. For each  $\epsilon$ , the coefficient of variation in the pixel distribution,  $A_\epsilon$ , is calculated using

$$A_\epsilon = \left( \frac{\sigma_\epsilon}{\mu} \right)^2 \quad (2)$$

where  $\sigma_\epsilon$  is the standard deviation and  $\mu$  is the average number of pixels per box for the same grid size. The lacunarity,  $L$ , is the mean value of  $A_\epsilon$  over all  $\epsilon$ . The size of the boxes used was varied to identify the cut-off distance ( $L_c$ ) above which, the structure becomes homogenous and the fractal scaling disappears ( $D_f = 2$ ).

## Results and discussion

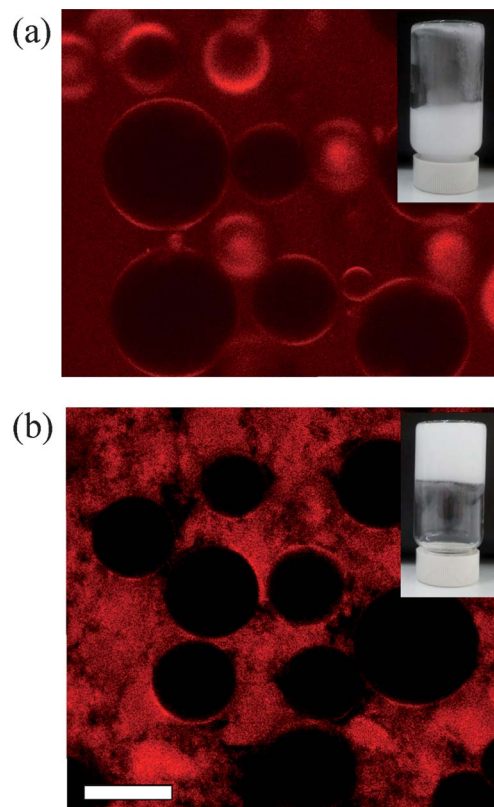
Coagulation of the laponite particles leads to complex structures in the emulsions as the interactions between the particles cause

rapid growth of large particle clusters. The oil droplets are trapped within these super-aggregate particulate structures. The resulting structure is a network of interconnected drops and particles that spans the whole emulsion volume, as shown in Fig. 2. The aggregate size varies with the salt concentration in the aqueous phase (Fig. 2). This super-aggregate structure has a critical influence on the emulsion breakdown and recovery behavior. The emulsions are solid-like materials which exhibit enhanced viscosity and yield stress compared to laponite dispersions alone. The dynamic rheological behaviour of the dispersions and emulsions in the linear viscoelastic regime was used to characterize the dispersions and emulsions at rest.

### Gelled laponite dispersion characterisation

Rheology measurements were initially made at different times after preparation of the laponite dispersions, to investigate the aging kinetics of the dispersions. The viscous flow and oscillatory response are reproducible after about 24 h, indicating that the fast aging processes in the dispersions were completed. Slower aging processes occur over a time period of several weeks.<sup>26</sup> All the results shown here were obtained within 72 h of preparation avoid any effect of the slow aging dynamics of the laponite dispersions.

The gelled laponite dispersions used to stabilise the emulsions exhibit a yield stress ( $\sigma_y$ ) and an elastic storage modulus,  $G'$ , which is much higher than their viscous loss modulus,  $G''$ .  $G'$



**Fig. 2** Confocal fluorescence images of the structure in 20 vol% bromohexadecane-in-water emulsions stabilized by 2 wt% particles at (a) 0.002 M and (b) 0.01 M NaCl. The scale bar corresponds to 50  $\mu\text{m}$ . Inset in each image is a photo of the emulsion in an inverted sample tube.

shows limited dependence on the frequency of the oscillatory stress being applied. The average value of  $G'$  increases with the particle concentration, as shown in Fig. 3. The particle concentration is plotted relative to the concentration at which gelation occurs for a given salt concentration.<sup>27</sup> The elasticity data scale with the reduced particle concentration as

$$G' = A(C_p - C_0)^\alpha \quad (3)$$

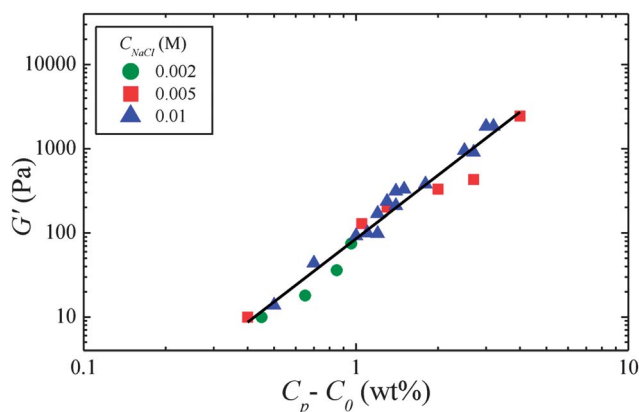
The scaling exponent ( $\alpha = 2.5$ ) does not depend on the clay or salt concentration. It is close to the exponents measured in earlier studies of laponite and of other clays, including nontronite and montmorillonite.<sup>28</sup> This power appears to be characteristic of all swelling clays.

Analysis of the dispersion yield stress values shows that they also fall on a master curve when plotted as a function of the reduced particle concentration ( $C_p - C_0$ ). The yield stress values are systematically lower than the elasticity values. The yield stress is a linear function of the elasticity as given by

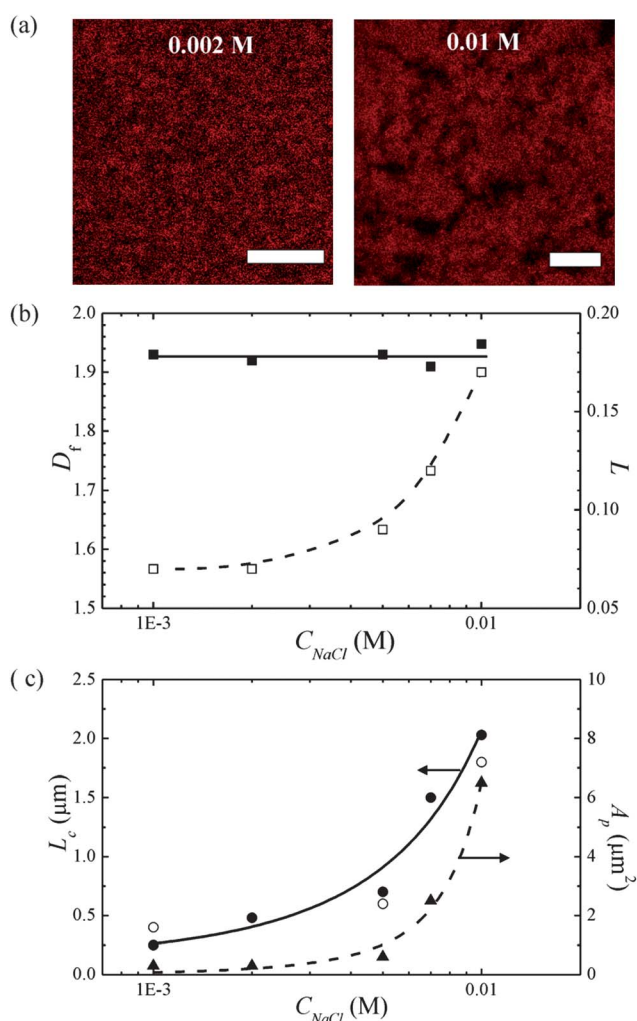
$$\sigma_y = G' \gamma_c \quad (4)$$

where  $\gamma_c$  is the critical strain of the dispersions.  $\gamma_c$  is typically about 0.1 for these laponite dispersions. Similar relationships have been observed between the yield stress and elasticity of other anisometric particles (nontronites, montmorillonites, hectorites, beidellites).<sup>28</sup>

The internal structure of the laponite gels was observed using confocal fluorescence microscopy. The laponite particles were stained with Rhodamine B. Heterogeneous structures with zones of denser and less dense particle aggregates are observed in images of laponite dispersions prepared at different salt concentrations, as shown in Fig. 4a. At rest, laponite particles aggregate into micrometre-sized domains. The loose connection of these micrometre-sized aggregates gives the continuous, three dimensional structures observed in the confocal images (Fig. 4a). The structures have a fractal dimension  $D_f \sim 1.9$  (Fig. 4b). These observations are consistent with the characteristic length scales



**Fig. 3** Particle concentration ( $C_p$ ) dependence of the laponite dispersion elastic modulus ( $G'$ ). The particle concentration is reduced by  $C_0$ , the solid fraction above which a viscoelastic gel appears. The salt concentration in the dispersions ( $C_{NaCl}$ ) is shown in the legend. The solid line corresponds to eqn (3) with  $\alpha = 2.5$ .



**Fig. 4** (a) Confocal fluorescence images of floc structure in 2 wt% laponite dispersions at the salt concentrations shown on the images. The scale bars correspond to 10  $\mu\text{m}$ . (b) Salt concentration ( $C_{NaCl}$ ) dependence of the fractal dimension ( $D_f$ ,  $\blacksquare$ ) and lacunarity ( $L$ ,  $\square$ ) of the coagulated particle networks formed the laponite dispersions. Lines are shown to guide the eye. (c) Salt concentration dependence of the maximum cut-off distance ( $L_c$ ,  $\bullet$ ,  $\circ$ ) and average pore area ( $A_p$ ,  $\blacktriangle$ ,  $\triangle$ ) of the coagulated particle networks formed in dispersions (filled symbols) and emulsions (open symbols). Lines are shown to guide the eye.

and fractal behavior deduced from neutron and light scattering studies of laponite dispersions.<sup>20</sup>

Although the fractal dimension remains the same, the particle network seems less homogeneous at higher salt concentrations. As the salt concentration increases, the rate of particle aggregation increases (shown later). The fractal character of the network is observed up to longer length scales, as shown by the increase in the upper spatial cut-off limit ( $L_c$ ) for the fractal scaling with the salt concentration (Fig. 4c). The size of the pores in the aggregates increases with the salt concentration (Fig. 4c). Another contributing factor is the coarser aggregate structures at higher salt concentrations which results in more variation in the pore shapes. Overall, these changes in the microstructure can be characterized by the lacunarity, which is a measure of the structural heterogeneity.<sup>29</sup> Lacunarity is used as a complimentary

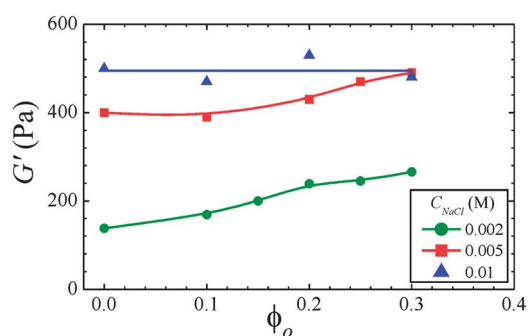
measurement to the fractal dimension.  $L$  is a measure of the variability in the pixel counts about the average values used in the standard box counting procedure to estimate  $D_f$ . Fig. 4b shows that the lacunarity increases with salt concentration as larger pores are incorporated into the particle networks.

### Laponite-stabilised emulsion characterisation

Emulsification times were set to obtain roughly similar drop size distributions (number average radius  $\sim 20 \mu\text{m}$ ) in the emulsions studied. The emulsions were diluted at constant particle and salt concentration to investigate the effect of oil volume fraction on the emulsion elasticity. The mechanical state of the laponite dispersions used to stabilise the emulsions was fixed by adjusting the laponite concentration relative to that required for gelation. This parameter depends only on the salt concentration in the dispersion. Typically the particle concentration was chosen to be close to that required for gelation. The maximum length scale at which the fractal character of the particle networks in the continuous phase of the emulsions was observed are similar to the spatial cut-off limits in the particle dispersions (Fig. 4c).

The elasticity values obtained for emulsions stabilized by 2wt% gelled laponite dispersions are summarized in Fig. 5a. The oil volume fraction dependence of the emulsion elasticity varies significantly with the salt concentration. At salt concentrations just above that required to cause gelation of the dispersions the emulsion elasticity increases with the drop volume fraction. At higher salt concentrations, the rheological behavior of the emulsions is dominated by the behavior of the coagulated laponite dispersions. There is less variation in  $G'$  with  $\phi_o$  at the oil volume fractions studied.

The emulsions show significant elasticity at drop volume fractions well below that required for close packing of the drops ( $\phi_m \sim 0.64$ ) due to the presence of the aggregated laponite particles in the emulsion continuous phase. Effectively, the emulsions behave as suspensions of large oil drops embedded in a gelled suspension of clay particles. Since the emulsion rheology is determined primarily by the flow behavior of the laponite dispersions, the emulsions can be treated as filled polymer gels. Assuming that the effective elastic modulus of the drops is larger than that of the laponite gel, then the reinforcement of the laponite gel strength by the drops will be a function of the drop volume fraction and the ratio of the droplet and dispersion

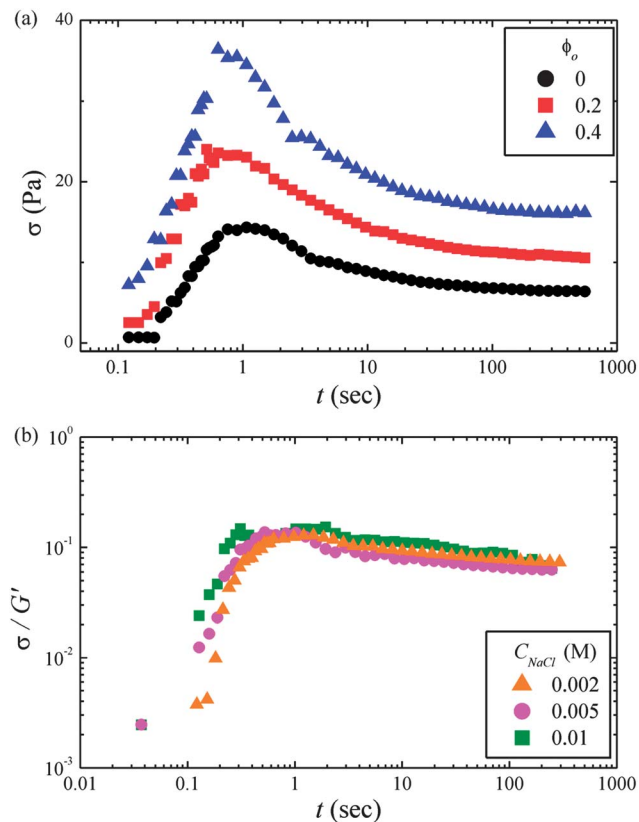


**Fig. 5** Volume fraction ( $\phi_o$ ) dependence of the elastic storage modulus ( $G'$ ) of emulsions stabilized by 2 wt% particles at different salt concentrations.

moduli.<sup>30</sup> Thus the influence of the oil droplets on the emulsion rheology decreases as the gel strength of the laponite dispersions increases (Fig. 5a). The kinetics of structure formation in the dispersions is relatively slow at low salt concentrations (shown later). It is possible that this enables greater incorporation of laponite particles attached to the drop surfaces into the super-aggregate structures formed by the laponite particles in the continuous phase of the emulsions. So the drops also are more efficient at enhancing the gel strength of laponite dispersions at lower salt concentrations. Dickinson and Chen<sup>30</sup> observed similar variations in the rheology of protein-stabilised emulsion gels with the protein gel strength.

### Emulsion thixotropy

The thixotropic behaviour of the emulsions is illustrated by two kinds of results: destruction of the network by shear and recovery after cessation of the shear. Fig. 6a shows the transient response of the emulsions when a constant shear rate is applied. The emulsions follow a curve that is characteristic of the dispersions used to stabilize the emulsions. At short times the stress increases linearly with time indicating that the emulsion deformation is elastic. The maximum stress reached is related to the yield stress of the emulsion. Beyond this maximum, the emulsions start to



**Fig. 6** (a) Time ( $t$ ) dependence of the shear stress ( $\sigma$ ) of emulsions at different oil volume fractions being sheared at a rate of  $5 \text{ s}^{-1}$ .  $C_p = 2 \text{ wt}\%$ ,  $C_{\text{NaCl}} = 0.002 \text{ M}$  NaCl. (b) Time dependence of the emulsion shear stress scaled by the elastic storage modulus ( $G'$ ) for emulsions prepared at different salt concentrations.  $\phi_o = 0.2$ ,  $C_p = 2 \text{ wt}\%$ .

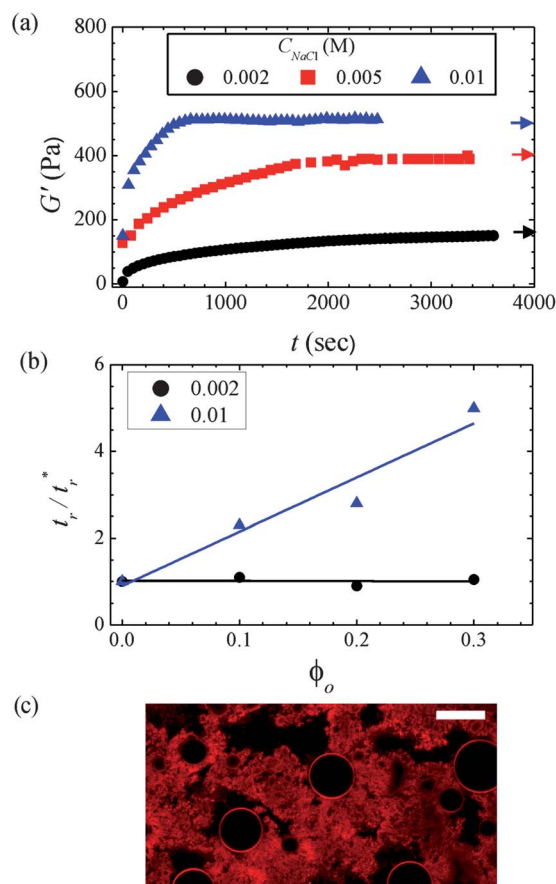
flow and the stress relaxes until a steady flow regime is reached. The decrease corresponds to breakdown of the network.<sup>31</sup>

The time-dependent changes in stress reveal two periods with distinct time scales in the breakdown process, situated on either side of the maximum stress and corresponding critical strain. The first period corresponds to elastic strain of the material and orientation of the structure. The second corresponds to flow and disaggregation of the structure. The order of magnitude of the time scale in the first period is shorter than that in the second. The relaxation behavior of the emulsions is slow, consistent with the presence of large scale structure formation in the emulsions observed in the confocal microscope images (Fig. 2). The first period lasts for about 1 s and the second up to 1000 s, giving a time scale ratio of 1/1000. The influence of shear rate on the characteristic times of breakdown was investigated by measuring the time-dependent changes in stress for various shear rates. The kinetics of breakdown differs depending on the shear rate applied, however, the ratio of the time scales remains about the same.

The maximum stress and the steady state stress reached when a constant shear rate is applied increase with the drop volume fraction in the emulsions. This occurs in particular for emulsions prepared at low salt concentrations, where the drops are more readily incorporated into the laponite super-aggregate structures. It is possible, however, to draw a master curve for these different relaxation curves by scaling the stress by the elastic storage modulus of the emulsion, as shown in Fig. 6b. Furthermore, all stress relaxation data for emulsions prepared at the same drop size could be normalized in this way (Fig. 6b). This means that the relaxation behaviour of laponite-stabilised emulsions is determined primarily by that of the dispersions used to stabilize the emulsions.

After breakdown measurements, the emulsions were subjected to a low-strain harmonic shearing so the kinetics of recovery could be monitored. The levels reached for  $G'$  (and  $G''$ ) increase with the salt concentration, as shown in Fig. 7a. The evolution in  $G'$  with time followed similar trends to that observed for the particle dispersions alone. Typically there are two periods in the recovery curves. The first period lasts up to a few minutes and the rate of increase in  $G'$  is several times faster than the second period, which takes up to 30 min. For a given emulsion, the maximum elasticity reached is consistent with the value measured in a dynamic oscillatory test.

The recovery of the emulsion elasticity is increasingly rapid as the salt concentration or the particle concentration increases. In particular, the kinetics of the increase in  $G'$  in the second period increase and hence the total time ( $t_r$ ) required to reach the final  $G'$  value decreases with increasing salt concentration, as shown in Fig. 7a. This is consistent with the large scale particle networks observed in the continuous phase of emulsions at high salt concentrations (Fig. 2). Importantly, incorporation of oil drops into highly elastic laponite dispersions can cause significant changes to the recovery behaviour. The recovery time can increase substantially as the drop volume fraction increases, as shown in Fig. 7b. This implies that recovery of the fractal character of the large scale structures (which are up to tens of micrometres in length) in the continuous phase of the emulsions prepared at high salt concentrations is hindered by the presence of drops (40  $\mu\text{m}$  in diameter). Examination of the structure in confocal fluorescence microscope images of these emulsions



**Fig. 7** (a) Time dependence of the elastic storage modulus ( $G'$ ) of emulsions at different salt concentrations after being sheared at a rate of  $50 \text{ s}^{-1}$  for 2 min. The arrows indicate the value of  $G'$  measured prior to shearing.  $C_p = 2 \text{ wt}\%$ ,  $\phi_o = 0.1$ . (b) Drop volume fraction dependence of the time taken to reach steady  $G'$  values ( $t_r$ ) for emulsions after shearing at a rate of  $10 \text{ s}^{-1}$ . The recovery time is scaled by that of the particle dispersion.  $C_p = 2 \text{ wt}\%$ . (c) Confocal fluorescence image of the structure in an emulsion at  $0.01 \text{ M NaCl}$  after shearing.

revealed that shearing disrupts the particle network structures, as shown in Fig. 7c. The extent of the network disruption increases with increasing strain on the emulsion during the breakdown period. This presumably produces a relatively homogeneous broken-down structure which can aggregate rather quickly. Thus recovery times tend to decrease as the shearing rate applied during breakdown increases. In contrast, recovery times for emulsions prepared at lower salt concentrations do not vary substantially with the drop volume fraction (Fig. 7b). Presumably, the smaller sized aggregate structures that form in these emulsions are more easily disrupted. Future experiments will investigate the role of the interactions between the droplet surfaces with the laponite network structures on structure recovery in the emulsions.

## Conclusions

Thixotropic emulsions were formed by stabilizing emulsions with laponite particles alone. They are hierarchically organized and consist of oil drops stabilized by laponite particles attached to their surfaces and incorporated into a three dimensional network

structure of particles. The laponite particles coagulate in the aqueous phase into dense microdomains that are connected into super-aggregates. The rate of aggregation and hence size of the aggregates is determined primarily by the salt concentration. The transient flow behavior of the emulsions reflects the complex structure of these systems. The mechanical properties of the emulsions depend on the mechanical properties of the laponite dispersions and the oil drop volume fraction.

## Acknowledgements

The particles were kindly supplied by Rockwood Additives Limited. We thank L. Waterhouse (Adelaide Microscopy, The University of Adelaide) for help with the confocal fluorescence microscopy experiments. CPW acknowledges receipt of an Australian Research Council Future Fellowship.

## References

- 1 H. A. Barnes, *J. Non-Newtonian Fluid Mech.*, 1997, **70**, 1.
- 2 J. Mewis and N. J. Wagner, *Adv. Colloid Interface Sci.*, 2009, **147–148**, 214.
- 3 C. H. Lee, V. Moturi and Y. Lee, *J. Controlled Release*, 2009, **136**, 88.
- 4 A. Ragouilliaux, G. Ovarlez, N. Shahidzadeh-Bonn, B. Herzhaft, T. Palermo and P. Coussot, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2007, **76**, 051408.
- 5 B. P. Binks, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 21.
- 6 E. Dickinson, *Curr. Opin. Colloid Interface Sci.*, 2010, **15**, 40.
- 7 F. Leal-Calderon and V. Schmitt, *Curr. Opin. Colloid Interface Sci.*, 2008, **13**, 217.
- 8 P. Coussot, H. Tabuteau, X. Chateau, L. Tocquer and G. Ovarlez, *J. Rheol.*, 2006, **50**, 975.
- 9 A. Fall, J. Paredes and D. Bonn, *Phys. Rev. Lett.*, 2010, **105**, 225502.
- 10 N. Monahan, Thesis, Victoria University of Wellington, 2010.
- 11 S. Abend, N. Bonnke, U. Gutschner and G. Lagaly, *Colloid Polym. Sci.*, 1998, **276**, 730.
- 12 J. Chen, R. Vogel, S. Werner, G. Heinrich, D. Clause and V. Dutschk, *Colloids Surf., A*, 2011, **382**, 238.
- 13 S. Simon, S. Theiler, A. Knudsen, G. Oye and J. Sjoblom, *J. Dispersion Sci. Technol.*, 2010, **31**, 632.
- 14 N. Sugita, S. Nomura and M. Kawaguchi, *J. Dispersion Sci. Technol.*, 2008, **29**, 931.
- 15 Y. Cui, M. Threlfall and J. S. van Duijneveldt, *J. Colloid Interface Sci.*, 2011, **356**, 665.
- 16 J. Thieme, S. Abend and G. Lagaly, *Colloid Polym. Sci.*, 1999, **277**, 257.
- 17 S. Zhang, D. Sun, X. Dong, C. Li and J. Xu, *Colloids Surf., A*, 2008, **324**, 1.
- 18 R. G. Avery and J. D. F. Ramsay, *J. Colloid Interface Sci.*, 1986, **109**, 448.
- 19 J. M. Saunders, J. W. Goodwin, R. M. Richardson and B. J. Vincent, *J. Phys. Chem. B*, 1999, **103**, 9211.
- 20 F. Pignon, A. Magnin, J. M. Piau, B. Cabane, P. Lindner and O. Diat, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 1997, **56**, 3281.
- 21 S. A. F. Bon and P. J. Colver, *Langmuir*, 2007, **23**, 8316.
- 22 S. Guillot, F. Bergaya, C. de Azevedo, F. Warmont and J.-F. Tranchant, *J. Colloid Interface Sci.*, 2009, **333**, 563.
- 23 J. Wang, G. Liu, L. Wang, C. Li, J. Xu and D. Sun, *Colloids Surf., A*, 2010, **353**, 117.
- 24 L. Rosta and H. R. Vongunten, *J. Colloid Interface Sci.*, 1990, **134**, 397.
- 25 D. W. Thompson and J. T. Butterworth, *J. Colloid Interface Sci.*, 1992, **151**, 236.
- 26 S. Bhatia, J. Barker and A. Mourchid, *Langmuir*, 2003, **19**, 532.
- 27 A. Mourchid, E. Lecolier, H. Van Damme and P. Levitz, *Langmuir*, 1998, **14**, 4718.
- 28 E. Paineau, L. J. Michot, I. Bihannic and C. Baravian, *Langmuir*, 2011, **27**, 7806.
- 29 T. G. Smith, G. D. Lange and W. B. Marks, *J. Neurosci. Methods*, 1996, **69**, 123.
- 30 E. Dickinson and J. S. Chen, *J. Dispersion Sci. Technol.*, 1999, **20**, 197.
- 31 F. Pignon, A. Magnin and J. M. Piau, *J. Rheol.*, 1998, **42**, 1349.

## A5. PROFITABILITY ANALYSIS

### A5.1. Project implementation budget

Table 5.1. Project implementation budget.

PE - Principal Equipment	Nr.Equipments	Costs Index	Estimated	Low	Probable	High
	26	2,34	620		1.454	
PEC - Principal Equipment Costs				1.309	1.454	1.599
NLEC - Not-Listed Equipment Costs	P&ID: Highly elaborated 2-10%, Preliminar 10-20%			65	73	80
BEC - Base Equipment Costs (no catalyts)				1.374	1.527	1.679
AC - Average Costs			56			
		Comentaries	Factors			
Basic Equipment Assembly		Average	9% 10% 12%			
Cimentations and structures		Av.- Steel to Carbon	6% 7% 8%			
Piping		Low- Liquids and Sold	7% 8% 9%			
Isolation equipment and piping		Low	5% 6% 7%			
Power + Lightning		Liquids	4% 5% 6%			
Instrumentation		Average	9% 10% 12%			
Not Accounted		Complicated Process	4% 5% 6%			
Buildings		Inside Equipment	21% 25% 29%			
Others						
Building services (% of building)						
Lightning	5%					
Airing and A/C	8%					
Heating	10%					
Piping	12%					
Others	5%					
Services Total	40%		9% 10% 12%			
Subtotal factors			73% 86% 99%			
Adjustment	Low High					
	5% -5%					
FC - Adjusment Factors Costs			77% 86% 94%	1.055	1.313	1.578
DC - Plant Limits Direct Costs				2.429	2.840	3.257
IC- Indirect Costs	29%	from Direct Costs		704	824	945
Subtotal				3.133	3.663	4.202
Unexpected	14%	from the Subtotal		439	513	588
BSC - Bringing into Service Costs				0	0	0
<b>CTI - Installation and Bringing into Service Costs</b>				<b>3.572</b>	<b>4.176</b>	<b>4.790</b>
			Range	86%	100%	115%
Author: P. Corbi				Project Nr.12141		

**A5.2. Income and costs**

Table 5.2. Annual income and cost (I).

<b>1. Income by Products and Subproducts Sales.</b>						
	Substance	Unit (Tm, m3..)	Production/ U.Product	Production (Unit/Year)	Price/Selling Costs (AUS\$/U.)	Income/ Costs
Final Products	Sunscreen	Tm		500	7500	3750000
	A	Tm		500	7500	3750000
	B	Tm		500	7500	3750000
Subproducts				0		0
<b>Total Income</b>						<b>11250000</b>

<b>2. Raw Materials, Auxiliary Materials, Catalysts and Processing Agents.</b>						
	Substance	Unit (Tm, m3..)	Consumption /Product U.	Total Consumption	Price (AUS\$/U.)	Costs
Materials	Deionezed water	Tm		912	3000	2736000
	Laponite XLG	Tm		12	5000	60000
	Gel White L	Tm		30	5000	150000
	Optigel WX	Tm		3	5000	15000
	Citric Acid	Tm		3	1700	5100
	Dow Corning	Tm		300	2800	840000
	TiO2	Tm		150	2700	405000
	Glycerine	Tm		7,5	2000	15000
	Dowicil 200	Tm		7,5	2000	15000
	Pure Thix HH	Tm		75	4000	300000
	<b>Total Costs MP+MA</b>					

<b>3.Plant services</b>						
	Unit (Tm, m3..)	Consumption Unit/Product Unit	Units/ Year	Variable AUS\$/ Unit	Variable Costs	Fix Fixed Costs
Cooling water	kg		18345304	0,17	3118701,68	
Electrical Energy	kWh		259992	0,123	31979,016	
Air instruments	m <sup>3</sup> N		10000	0,007	70	
N <sub>2</sub>	m <sup>3</sup> N		2000	0,05	100	
<b>Services total</b>					<b>3150851</b>	<b>0</b>

Table 5.2. Annual income and cost (II).

<b>4. Human Resources Costs</b>			
Type	Nº People	Av. Cost per Unit	Costs
Operation	30	48600	1458000
Laboratory	1	35640	35640
Admin	1	36000	36000
Others	2	32400	64800
			1594440

<b>5. Maintenance and Structure Costs</b>			
	Total Investment Costs (TIC)	Installation Type Factor	
Maintenance	4.176.066	2,5%	104402
	Estructural Costs	Repercussion Factor	
Structure		0,0%	0
			104402

<b>6. Circulating Capital</b>			
Inventories	Unit (Tm, m3..)	Price (Euros/U.)	Circulating Capital
Raw and Aux. Mats.			
CCC			0
EEE			0
Products			
AAA			0
Subproducts			
BBB			0
Catalysts			0
Inventory Total			0

<b>7. Amortizations</b>			
	Lifetime	Capital	Amortization
Buildings	0	0	0
Equipments/instalat.	26	4.176.066	160617,9044
Short-life equipments	0	0	0
Total		4176066	160618

### A5.3. Global investment evaluation

Table 5.3. Results of global investment evaluation.

Year	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022
% Production Capacity		80%	85%	90%	95%	100%	100%	100%	100%	100%	100%
Capital Investment	4,176										
Income		9,00	9,56	10,13	10,69	11,25	11,25	11,25	11,25	11,25	11,25
Variable Costs		6,15	6,54	6,92	7,31	7,69	7,69	7,69	7,69	7,69	7,69
Fixed Costs		1,70	1,70	1,70	1,70	1,70	1,70	1,70	1,70	1,70	1,70
Inventory Variation		0,00									
EBIT, Profit and Loss Account		1,15	1,33	1,50	1,68	1,86	1,86	1,86	1,86	1,86	1,86
Amortization		0,16	0,16	0,16	0,16	0,16	0,16	0,16	0,16	0,16	0,16
Taxes	30%	0,30	0,35	0,40	0,46	0,51	0,51	0,51	0,51	0,51	0,51
Cash-Flow		-4,2	0,9	1,0	1,1	1,2	1,3	1,3	1,3	1,3	1,3
Cash-Flow Accumulated		-4,2	-3,3	-2,3	-1,2	0,0	1,3	2,7	4,0	5,4	6,7
Discounted C-Flow (DCF)	1,0%	-4,18	0,85	0,97	1,08	1,19	1,30	1,28	1,26	1,25	1,23
Discounted C-Flow (DCF)	3,0%	-4,18	0,85	0,95	1,04	1,12	1,20	1,16	1,13	1,10	1,03
<b>Discounted C-Flow (DCF)</b>	<b>9,0%</b>	<b>-4,18</b>	<b>0,85</b>	<b>0,90</b>	<b>0,93</b>	<b>0,95</b>	<b>0,96</b>	<b>0,88</b>	<b>0,74</b>	<b>0,68</b>	<b>0,62</b>
<b>Discounted C-Flow (DCF)</b>	<b>32,7%</b>	<b>-4,18</b>	<b>0,85</b>	<b>0,74</b>	<b>0,62</b>	<b>0,52</b>	<b>0,43</b>	<b>0,33</b>	<b>0,25</b>	<b>0,19</b>	<b>0,11</b>
Acc. DCF €M	1,0%	-4,18	0,85	1,82	2,90	4,09	5,38	6,67	7,94	9,20	10,44
Acc. DCF €M	3,0%	-4,18	0,85	1,80	2,84	3,96	5,16	6,32	7,45	8,55	9,61
<b>Acc. DCF €M</b>	<b>9,0%</b>	<b>-4,18</b>	<b>0,85</b>	<b>1,75</b>	<b>2,67</b>	<b>3,62</b>	<b>4,58</b>	<b>5,45</b>	<b>6,26</b>	<b>7,00</b>	<b>7,67</b>
<b>Acc. DCF €M</b>	<b>32,7%</b>	<b>-4,18</b>	<b>0,85</b>	<b>1,59</b>	<b>2,21</b>	<b>2,74</b>	<b>3,17</b>	<b>3,50</b>	<b>3,74</b>	<b>3,93</b>	<b>4,07</b>
Interest % Net Present Value											
NPV	1,0%	-4,18	-3,32	-2,36	-1,28	-0,09	1,21	2,49	3,76	5,02	6,27
NPV	3,0%	-4,18	-3,32	-2,38	-1,34	-0,22	0,98	2,14	3,28	4,37	5,44
NPV	<b>9,0%</b>	<b>-4,18</b>	<b>-3,32</b>	<b>-2,43</b>	<b>-1,50</b>	<b>-0,56</b>	<b>0,40</b>	<b>1,28</b>	<b>2,08</b>	<b>2,82</b>	<b>3,50</b>
Internal Rate of Return (IRR)											
NAV=0; IRR%	<b>32,7%</b>	<b>-4,18</b>	<b>-3,32</b>	<b>-2,59</b>	<b>-1,44</b>	<b>-1,01</b>	<b>-0,68</b>	<b>-0,43</b>	<b>-0,25</b>	<b>-0,11</b>	<b>0,00</b>

## **A6. THE SUNSCREEN INDUSTRY IN AUSTRALIA: PAST, PRESENT, AND FUTURE**

### **A6.1. Introduction**

With its prolonged periods of intense solar radiation the environment in Australia is such, that its predominantly white populations should take measures to provide adequate protection against the damaging effects of excessive exposure to sunlight. Only since the early 1970s, however, have the interest of industry and government been sufficient to generate an awareness of the significant role that sunscreen can play in providing this protection. As a consequence of publications by investigators, publicity releases by health authorities, and sales tax incentives provided by the government to manufacturers and suppliers to encourage development, Australia now has a wide range of highly effective sunscreens available.

Medical authorities have long recognized that the incidence of nonmelanoma skin cancer in Australia is among the highest in the world.

### **6.2. Standards Australia and sunscreens**

Standards Australia is, as the title indicates, a government-regulated body charged with developing standards for a wide variety of materials and operations. As the result of an approach to the government by an international manufacturer of sunscreens concerned about the supposedly poor quality of some of the sunscreens available, this association was asked by the Federal Department of Health to undertake the development of a procedure that could be used for determining the effectiveness of sunscreens.

As a consequence of this request Subcommittee 42 of the Standards Association was formed consisting of representatives of government, cosmetic and pharmaceutical manufactures, professional associations, and universities.

This committee met at regular intervals over several years. After considerable discussion Australian Standard 2604-1983 was finalized. The procedure finally accepted by the committee was a standardized version of the technique originally proposed by Schulde.

In Addition to providing a method of evaluation, this publication also gave directions for the labelling of sunscreens.

The test procedure proposed by Australian Standard 2604-1983 was essentially identical with that proposed for adoption by the U.S. Food and Drug Administration (FDA). In both procedures the xenon arc lamp was recommended as the preferred source of radiation. Unlike the FDA-proposed protocol, however, its Australian counterpart makes no provisions for testing sunscreens using natural sunlight. However, in the critical area of film thickness, which can significantly influence the results obtained, both procedures require the application of 2 mg/cm<sup>2</sup>m. Table 1 compares the major steps in the two procedures.

In 1986 a revised standard was published as Australian Standard 2604-1986. The title of the standard remained the same as that of the 1983 version, that is, “Sunscreen Products - Evaluation and Classification”. This version of the standard differed from the original by introducing the concept of the “secondary sunscreen”. This descriptive term was introduced, supposedly, to clarify the requirements for multipurpose sunscreen product relative to labelling. This revision of the standard also contained guidelines for the testing of both broad-spectrum and water-resistant products as did the 1983 edition.

Table 6.1. A comparison of the U.S. and Australian Procedures for the Determination of the SPF.

<b>Parameter</b>	<b>United States</b>	<b>Australia</b>
No of panelists	20	10
Preferred radiation source	Xenon arc	Xenon arc
Product dose (mg/cm <sup>2</sup> )	2	2
Exposure increment (n)	1.25	1.25
Water resistance (min)	40	40
Waterproof (min)	80	not used
Standard test formula <sup>a</sup>	Yes	Yes

<sup>a</sup>The same standard formula is used in both procedures.

The latest edition of Australian Standard 2604 was published in 1993 as a joint publication between Standards Australia and Standards New Zealand. New Zealand sunscreen suppliers must now provide only products that comply with this new publication, known as Australian/New Zealand Standard 2604-2993, if they wish their product to be included in a list of sunscreens published by the New Zealand government. This marks the initiation of regulations for the sunscreen industry in New Zealand.

### **A6.3. Sunscreen products: evaluation and classification**

Australian Standard 2604-1993 describes procedures for determining the performance of sunscreens in term of their sun protection factor as did the two previous editions of the standard. As indicated previously, it also provides guidance in the testing of both broad-spectrum and water-resistant sunscreen products. The standard also specifies labelling requirements in some detail. The following sections describe more fully the precise requirements applying to sunscreens as indicated in the standard.

### **A6.4. Classification of sunscreens**

Sunscreens in Australia are classified either as primary or as secondary sunscreen products. This is a somewhat arbitrary division of these preparations into those that have as their main or primary function the protection of the skin against the effects of ultraviolet radiation and those products that are primarily intended to serve some other purpose, but contain an ultraviolet absorber as an additive action to their main functions.

The description of a product as a “sunscreen with added moisturizer” would designate the preparation as a primary sunscreen. Alternatively, if the product is described as a “moisturizer with added sunscreen”, the classification would be as a secondary sunscreen. The parameters that differentiate products into either of these two categories have never been defined.

The principal reason for establishing the two categories initially was to overcome the concern of cosmetic manufacturers that some cosmetics, such as lipsticks, would not have room on their container to include all the labelling requirements that a primary sunscreen must meet.

### **A6.5. Sunscreen Categories**

Both primary and secondary sunscreen products are classified into four categories, based on the label SPF value. These category descriptions are shown in Table 2. Products with a protection factor of less than 2 are not considered to be sunscreens.

In the first two editions of Australian Standard 2604 it was mandatory that the sunscreen label must display the sunscreen category into which the product fell. The Australia-New Zealand Standard 2604-1993 has removed the requirement that the sunscreen category must be shown on the label. In the opinion of the SPF value that the category designation had become superfluous. The SPF value is now the only mandatory requirement of a sunscreen label relative to the level of effectiveness provided.

The 1993 standard also saw the category description of “maximum” changed to the designation “very high protection”. It was felt that the term maximum implied “absolute” protection and, therefore, was not appropriate. A further change in categories was the elimination in the 1993 edition of the table relating the category description to skin type. This change was made because it was considered that this advice was no longer appropriate, as it could be interpreted that people with category IV skins and above would not benefit from a higher SPF product.

**A6.6. Broad-spectrum sunscreens**

The term Broad-spectrum is used in Australia to describe those products that, in addition to providing protection in the UVB region between 280 and 320 nm, also provide protection against UVA radiation higher than 320nm. The original standard published in 1983 restricted the use of this term solely to sunscreens that were described at that time as providing maximum protection. In the 1986 standard, however, this terminology was extended so that it could be applied to sunscreens categorized as moderate and high protection also. Sunscreens with SPF values of less than 4, which are considered to be minimum protection products, cannot be described as having broad-spectrum capabilities.

Table 5.2 Categorization of sunscreens in Australia

<b>Category</b>	<b>SPF level</b>
Minimum protection	At least 2, but < 4
Preferred radiation source	At least 4, but < 8
Product dose (mg/cm <sup>2</sup> )	At least 8, but < 15
Exposure increment (n)	15 or more <sup>a</sup>

<sup>a</sup> Australian standards state that products with SPF values greater than 15 may only be labelled SPF 15+.

**A6.7. Water-Resistant Sunscreens**

The Australian standard outlines procedures that can be used for determining the water-resistance of a sunscreen. As an example, there is a definite anomaly in stating on the label of an SPF 4 product that it is water resistant for up to 4 or even 8 h. Because the times claimed for water resistance should not exceed the times for which the sunscreen would be expected to give adequate protection. Australian Standard has placed limits on the length of time immersed that may be claimed for a water-resistant sunscreen. Table 3 shows these limits.

The term waterproof is not merited under current regulations. The product may be described only as being water-resistant, regardless of the period of immersion to which it might have been subjected.

**6.8. Government regulations**

Before 1992, sunscreens in Australia were considered to be in the same category as cosmetic, and regulations governing the marketing of such products were the concern of the various state governments. In 1992, sunscreens were declared to be drugs and came under the control of the Therapeutic Goods Administration (TGA), a division of the Federal Department of Health.

Table 5.3 Water-Resistance Claims.

<b>SPF value after immersion</b>	<b>Maximum water-resistance claimed</b>
At least 2, but < 4	Shall not be claimed
At least 4, but < 8	1h
At least 8, but 15	2h
15 or more	4h

As a consequence of this development, sunscreens are under more rigid control than they previously were, In addition to ensuring that the product complies with the current Australian standard the manufacturer must comply with the Code of Good Manufacturing Practice. The active ingredients must be stated on the label, and only those ingredients that have been recognized in various government regulations are permitted. In addition, sunscreen must now carry an expiration date, similar to other drug products.

**A6.9. Anticancer councils and sunscreens**

The knowledge that the incidence of skin cancer has almost reached epidemic proportions in Australia has led to concerted efforts by government health departments and anticancer organizations to increase public awareness of the dangers associated with unwise exposure to sunlight.

To encourage manufacturers to market sunscreens, and also to keep the cost of these within the reach of lower-income families, the Australian government exempts from sales tax all primary sunscreens showing effectiveness level of SPF 4 or higher. Anticancer councils in each of the states are very active in their fight against skin cancer.

**A6.10. Sunscreens in the future**

Since 1970, there has been a tremendous increase in our knowledge of the relation between exposure to ultraviolet radiation and skin damage. In the last decade the development of daytime moisturizers and other products of a cosmetic nature containing ultraviolet absorbers have increased significantly.

All this information was found in (ref. 5).

# SAFETY DATA SHEET



## 1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY/UNDERTAKING

**Identification of the substance/preparation** Laponite® XLG

**Version #** 01

**Revision Date** 08-20-2008

**Manufacturer information EU** Rockwood Additives  
Moorfield Road, Widnes  
WA8 3AA  
United Kingdom  
msdsinfo@rockwoodadditives.com  
Customer Service +44 (0)151 495-9871  
Emergency Number +49 (0) 6132 - 84463

**Manufacturer information** Southern Clay Products, Inc.  
1212 Church Street  
Gonzales, TX 78629 US  
msdsinfo@scprod.com  
www.scprod.com  
Customer Service +1 (830) 672 - 2891  
CHEMTREC (INTERNATIONAL) +1 (703) 527 - 3887  
CHEMTREC (US) (800) 424 - 9300

**Product Use** Laponite® products are used to control viscosity and flow properties in water based formulations such as toothpaste, paint, personal care and household cleaning products. Laponite® can impart shear sensitive viscosity and improve syneresis control. Laponite® products are also used to produce antistatic coatings.

## 2. HAZARDS IDENTIFICATION

This substance is not classified as dangerous according to Directive 67/548/EEC.

**Physical hazards** Not classified as a physical hazard.

**Health hazards** Not classified as a health hazard.

**Environmental hazards** Not classified as an environmental hazard.

**Specific hazards** Material can be slippery when wet.

## 3. COMPOSITION/INFORMATION ON INGREDIENTS

Components	CAS #	Percent	EC-No.	Classification
Silicic Acid, Lithium Magnesium Sodium Salt	53320-86-8	99 - 100	258-476-2	

## 4. FIRST AID MEASURES

**Inhalation** Move to fresh air. Call a physician if symptoms develop or persist.

**Skin contact** Wash off with soap and water. Get medical attention if irritation develops or persists.

**Eye contact** Flush eyes with water as a precaution. Get medical attention if irritation develops or persists.

**Ingestion** If ingestion of a large amount does occur, seek medical attention. Rinse mouth with water.

**General advice** No hazards which require special first aid measures.

## 5. FIRE-FIGHTING MEASURES

**Fire fighting equipment/instructions** Use any media suitable for the surrounding fires. Not a fire hazard.

**Unusual fire & explosion hazards** Not a fire hazard. None known.

**Specific hazards** Not a fire hazard. The product itself does not burn. Material can be slippery when wet

## 6. ACCIDENTAL RELEASE MEASURES

**Personal precautions** Local authorities should be advised if significant spillages cannot be contained. Keep unnecessary personnel away. Avoid inhalation of dust from the spilled material. Wear a dust mask if dust is generated above exposure limits.

**Environmental precautions** Do not flush into surface water. Do not let product enter drains. Prevent further leakage or spillage if safe to do so.

<b>Containment procedures</b>	Avoid allowing water runoff to contact spilled material. If sweeping of a contaminated area is necessary use a dust suppressant agent which does not react with the product. Contaminated surfaces will be extremely slippery.
<b>Methods for cleaning up</b>	Sweep up or gather material and place in appropriate container for disposal. Collect dust or particulates using a vacuum cleaner with a HEPA filter. Avoid dust formation. After removal flush contaminated area thoroughly with water.

## 7. HANDLING AND STORAGE

<b>Handling</b>	Keep formation of airborne dusts to a minimum. Provide appropriate exhaust ventilation at places where dust is formed. Do not breathe dust from this material. Avoid contact with eyes. In case of insufficient ventilation, wear suitable respiratory equipment.
<b>Storage</b>	Guard against dust accumulation of this material. Keep in a well-ventilated place. Keep container tightly closed.

## 8. EXPOSURE CONTROLS/PERSONAL PROTECTION

### Occupational exposure limits

#### Belgium

Additional components	Type	Value	Form
Nuisance Particulates (seq250)	TWA	3 mg/m <sup>3</sup> 10 mg/m <sup>3</sup>	Respirable fraction. Inhalable fraction.

#### Bulgaria

Additional components	Type	Value	Form
Nuisance Particulates (seq250)	TWA	3.5 mg/m <sup>3</sup> 5 mg/m <sup>3</sup>	Respirable fraction. Inhalable fraction.

#### Estonia

Additional components	Type	Value	Form
Nuisance Particulates (seq250)	TWA	5 mg/m <sup>3</sup> 5 mg/m <sup>3</sup> 3 mg/m <sup>3</sup>	Respirable dust. Total dust. Dust.

#### Finland

Additional components	Type	Value
Nuisance Particulates (seq250)	TWA	10 mg/m <sup>3</sup>

#### France

Additional components	Type	Value	Form
Nuisance Particulates (seq250)	VME	5 mg/m <sup>3</sup> 10 mg/m <sup>3</sup>	Respirable fraction. Inhalable fraction.

#### Germany

Additional components	Type	Value	Form
Nuisance Particulates (seq250)	AWG	3 mg/m <sup>3</sup> 10 mg/m <sup>3</sup>	Respirable dust. Inhalable dust.

#### Hungary

Additional components	Type	Value	Form
Nuisance Particulates (seq250)	TWA	10 mg/m <sup>3</sup> 6 mg/m <sup>3</sup>	Total inhalable dust. Respirable dust.

#### Ireland

Additional components	Type	Value	Form
Nuisance Particulates (seq250)	TWA	10 mg/m <sup>3</sup> 4 mg/m <sup>3</sup>	Total inhalable dust. Respirable dust.

#### Italy

Additional components	Type	Value	Form
Nuisance Particulates (seq250)	TWA	3 mg/m <sup>3</sup>	Respirable particles.

<b>Additional components</b>	<b>Type</b>	<b>Value</b>	<b>Form</b>
		10 mg/m3	Inhalable particles.
<b>Latvia</b>			
<b>Additional components</b>	<b>Type</b>	<b>Value</b>	<b>Form</b>
Nuisance Particulates (seq250)	TWA	8 mg/m3	Aerosol
<b>Lithuania</b>			
<b>Additional components</b>	<b>Type</b>	<b>Value</b>	<b>Form</b>
Nuisance Particulates (seq250)	TWA	5 mg/m3 5 mg/m3 1 mg/m3	Inhalable fraction. Respirable fraction. Dust.
<b>Netherlands</b>			
<b>Additional components</b>	<b>Type</b>	<b>Value</b>	<b>Form</b>
Nuisance Particulates (seq250)	Ceiling	5 mg/m3 10 mg/m3	Respirable dust. Inhalable dust.
<b>Poland</b>			
<b>Additional components</b>	<b>Type</b>	<b>Value</b>	<b>Form</b>
Nuisance Particulates (seq250)	TWA	6 mg/m3 2 mg/m3	Total dust. Respirable dust.
<b>Portugal</b>			
<b>Additional components</b>	<b>Type</b>	<b>Value</b>	<b>Form</b>
Nuisance Particulates (seq250)	TWA	3 mg/m3 10 mg/m3	Respirable fraction. Inhalable fraction.
<b>Slovakia</b>			
<b>Additional components</b>	<b>Type</b>	<b>Value</b>	<b>Form</b>
Nuisance Particulates (seq250)	TWA	6 mg/m3 2 mg/m3 2 mg/m3 10 mg/m3 10 mg/m3	Aerosol Respirable aerosol fraction Respirable fraction. Total
<b>Spain</b>			
<b>Additional components</b>	<b>Type</b>	<b>Value</b>	<b>Form</b>
Nuisance Particulates (seq250)	TWA	3 mg/m3 10 mg/m3	Respirable fraction. Inhalable fraction.
<b>Sweden</b>			
<b>Additional components</b>	<b>Type</b>	<b>Value</b>	<b>Form</b>
Nuisance Particulates (seq250)	TWA	5 mg/m3 10 mg/m3	Respirable dust. Inhalable dust.
<b>United Kingdom</b>			
<b>Additional components</b>	<b>Type</b>	<b>Value</b>	<b>Form</b>
Nuisance Particulates (seq250)	TWA	4 mg/m3 10 mg/m3	Respirable dust. Inhalable dust.

#### Engineering measures

Ventilation should be sufficient to effectively remove and prevent buildup of any dusts or fumes that may be generated during handling or thermal processing. General ventilation normally adequate. If material is ground, cut, or used in any operation which may generate dusts, use appropriate local exhaust ventilation to keep exposures below the recommended exposure limits. If these are not sufficient to maintain concentrations of particulates and solvent vapour below the OEL, suitable respiratory protection must be worn.

## Personal protective equipment

<b>Respiratory protection</b>	If airborne concentrations are above the applicable exposure limits, use NIOSH approved respiratory protection.
<b>Hand protection</b>	PVC or other plastic material gloves.
<b>Eye protection</b>	Wear safety glasses with side shields.
<b>Skin and body protection</b>	Normal work clothing (long sleeved shirts and long pants) is recommended.
<b>General</b>	Not normally needed.

**Hygiene measures** Do not breathe dust. Avoid contact with eyes. Handle in accordance with good industrial hygiene and safety practice.

## 9. PHYSICAL AND CHEMICAL PROPERTIES

<b>Physical state</b>	Solid.
<b>Form</b>	Powder.
<b>Colour</b>	White.
<b>Odour</b>	Odourless.
<b>pH</b>	9.8 , 2% aqueous dispersion
<b>Melting point</b>	900 °C (1652 °F) estimated
<b>Freezing point</b>	Not applicable
<b>Boiling point</b>	Not applicable
<b>Flash point</b>	Not applicable
<b>Flammability limits in air, upper, % by volume</b>	Not applicable
<b>Flammability limits in air, lower, % by volume</b>	Not applicable
<b>Vapour pressure</b>	Not applicable
<b>Vapour density</b>	Not applicable
<b>Bulk density</b>	700 - 1300 kg/m <sup>3</sup>
<b>Relative density</b>	Not available.
<b>Solubility (water)</b>	Insoluble, forms a colloid gel
<b>Percent volatile</b>	0 % estimated

## 10. STABILITY AND REACTIVITY

<b>Conditions to avoid</b>	None known.
<b>Hazardous decomposition products</b>	No hazardous decomposition products are known.
<b>Stability</b>	Stable at normal conditions.
<b>Materials to avoid</b>	Strong oxidizing agents. Strong acids.
<b>Hazardous polymerisation</b>	Hazardous polymerisation does not occur.

## 11. TOXICOLOGICAL INFORMATION

### Toxicological data

Components	Test Results
Silicic Acid, Lithium Magnesium Sodium Salt (53320-86-8)	Acute Dermal PII rabbit: 0,5 Acute Inhalation LC50 rat: > 1660 mg/m <sup>3</sup> Acute Oral LD50 rat: > 8 g/kg

\* Estimates for product may be based on additional component data not shown.

<b>Routes of exposure</b>	Inhalation. Eye contact.
<b>Skin contact</b>	None known.
<b>Eye contact</b>	None known.
<b>Further information</b>	This product has no known adverse effect on human health.

## 12. ECOLOGICAL INFORMATION

<b>Ecotoxicity</b>	This material is not expected to be harmful to aquatic life.
<b>Environmental Effects</b>	An environmental hazard cannot be excluded in the event of unprofessional handling or disposal.
<b>Persistence and degradability</b>	None known. The methods for determining the biological degradability are not applicable to inorganic substances. Not inherently biodegradable.

### 13. DISPOSAL CONSIDERATIONS

**Disposal instructions** Dispose in accordance with all applicable regulations.  
**Waste from residues / unused products** Not applicable.  
**Contaminated packaging** Empty containers can be landfilled, when in accordance with the local regulations.

### 14. TRANSPORT INFORMATION

**ADR**  
Not regulated as dangerous goods.  
**IATA**  
Not regulated as dangerous goods.  
**IMDG**  
Not regulated as dangerous goods.

### 15. REGULATORY INFORMATION

**International regulations** The product does not need to be labelled in accordance with EC directives or respective national laws. This Safety Data Sheet complies with the requirements of Regulation (EC) No 1907/2006.  
This product is in compliance with Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronics equipment (RoHS).  
**Water hazard class** WGK 1

#### Inventory status

Country(s) or region	Inventory name	On inventory (yes/no)*
Australia	Australian Inventory of Chemical Substances (AICS)	yes
Canada	Domestic Substances List (DSL)	yes
Canada	Non-Domestic Substances List (NDSL)	no
China	Inventory of Existing Chemical Substances in China (IECSC)	yes
Europe	European Inventory of New and Existing Chemicals (EINECS)	yes
Europe	European List of Notified Chemical Substances (ELINCS)	no
Japan	Inventory of Existing and New Chemical Substances (ENCS)	yes
Korea	Existing Chemicals List (ECL)	yes
New Zealand	New Zealand Inventory	yes
Philippines	Philippine Inventory of Chemicals and Chemical Substances (PICCS)	yes
United States & Puerto Rico	Toxic Substances Control Act (TSCA) Inventory	yes

A "Yes" indicates that all components of this product comply with the inventory requirements administered by the governing country(s)

### 16. OTHER INFORMATION

**Disclaimer** MANUFACTURER DISCLAIMER: The information given within this SDS is correct to the best of our knowledge, information and belief at the date of its revision and publication. However, the manufacturer makes no representation, warranty or guarantee as to its accuracy, reliability or completeness, nor assumes any liability for its use. It is the user's responsibility to confirm in advance that the information is current, applicable and suitable to their circumstances for each particular use. No representative of ours has authority to waive this provision. Please call for document accuracy if the revision date has exceeded 3 years.  
**Issue date** 08-20-2008

**Dow Corning Australia Pty Ltd  
Material Safety Data Sheet****DOW CORNING 200(R) FLUID, FOODGRADE, 350 CST****STATEMENT OF HAZARDOUS NATURE:**

Not classified as hazardous according to criteria of Worksafe Australia.

**1. COMPANY DETAILS**

- 1.1 Company:** Dow Corning Australia Pty Ltd, ABN 36 008 444 166  
**1.2 Address:** Locked Bag 2095, North Ryde, NSW 1670, Australia  
**1.3 Telephone Number:** 1300-360-732  
**1.4 Emergency Telephone Number (within Australia):** 1300-360-732  
**(from outside Australia):** 61-1300-360-732

**2. Identification**

- 2.1 Product Name:** DOW CORNING 200(R) FLUID, FOODGRADE, 350 CST  
**2.2 Other Name:** Silicone  
**2.3 Manufacturer's Product Code:** 02251558  
**2.4 Correct Shipping Name:** Not applicable.  
**2.5 UN No.:** Not applicable.  
**2.6 Dangerous Goods (Class and Subs Risk):** Not applicable.  
**2.7 IATA Dangerous Goods Class:** Not subject to IATA regulations.  
**2.8 IMDG Dangerous Goods Class:** Not subject to IMDG code.  
**2.9 Hazchem Code:** Not applicable.  
**2.10 Poisons Schedule Number:** Not applicable.  
**2.11 Use:** Pharmaceutical additive  
Processing aid  
Antifoam  
Release agent  
Cosmetic additive

**2.12 Physical Description/Properties**

- Physical Form: Liquid  
Colour: Colorless  
Odour: Odorless  
Boiling Point: > 35C/95F  
Melting Point: Not determined.  
Vapour Pressure: Not determined.  
Specific Gravity @ 25°C: 0.97  
Flash Point: > 100 °C  
Lower Flammability Limit: Not determined.  
Upper Flammability Limit: Not determined.  
Solubility in Water: Not determined.  
Volatile Content: Not determined.

**Dow Corning Australia Pty Ltd  
Material Safety Data Sheet****DOW CORNING 200(R) FLUID, FOODGRADE, 350 CST****2.13 Other Properties**

Viscosity:	350 cSt
Vapour Density:	Not determined.
pH:	Not determined.
Autoignition temperature:	Not determined.

The above information is not intended for use in preparing product specifications. Contact Dow Corning before writing specifications.

**2.14 Ingredients:**

Chemical Name	CAS Number	Proportion %
Polydimethylsiloxane	63148-62-9	>60
Dimethyl cyclosiloxanes	69430-24-6	<1

**3. Health Hazard Information****3.1 Health Effects***Acute*

Ingestion:	Low ingestion hazard in normal use.
Eye:	Direct contact may cause temporary redness and discomfort.
Skin:	No significant irritation expected from a single short-term exposure.
Inhalation:	No significant effects expected from a single short-term exposure.

*Chronic*

Ingestion:	Repeated ingestion or swallowing large amounts may injure internally.
Skin:	No known applicable information.
Inhalation:	No known applicable information.

**3.2 Mutagenic Effects:**

None known.

**3.3 Reproductive Effects:**

Dimethyl cyclosiloxanes

**3.4 Carcinogenic Effects:**

None known.

**3.5 Other Health Hazard Information:**

No known applicable information.

The above listed potential effects of overexposure are based on actual data, the results of studies performed upon similar compositions, component data, and/or expert review of the products.

**3.6 First Aid**

Ingestion:	Get medical attention.
Eye:	Immediately flush with water.
Skin:	No first aid should be needed.

**Dow Corning Australia Pty Ltd  
Material Safety Data Sheet****DOW CORNING 200(R) FLUID, FOODGRADE, 350 CST**

Inhalation:	No first aid should be needed.
First Aid Facilities:	None should be required.
Comments:	Treat symptomatically.
Advice to Doctor:	Treat Symptomatically. For further information, the Medical Practitioner should contact Dow Corning Australia Pty Ltd.

**4. Precautions for Use****4.1 Exposure Standards:****Ingredients****Exposure Limits**

Dimethyl cyclosiloxanes

Dow Corning guide: TWA 10 ppm.

**4.2 Engineering Controls**Local Exhaust:  
General Ventilation:None should be needed.  
Recommended.**4.3 Personal Protection**Respiratory:  
Suitable Respirator:  
Hand:  
Eye:  
Skin:  
Personal Hygiene:No respiratory protection should be needed.  
None should be needed.  
No special protection needed.  
Use proper protection - safety glasses as a minimum.  
Washing at mealtime and end of shift is adequate.  
Exercise good industrial hygiene practice. Wash after handling, especially before eating, drinking or smoking.

Note: These precautions are for room temperature handling. Use at elevated temperature or aerosol/spray applications may require added precautions.

**4.4 Flammability**

Fire Hazards (precautions to be taken in handling and storage):

Use reasonable care and store away from oxidizing materials.

Unusual Fire Hazards:

None.

**5. Safe Handling Information****5.1 Advice on Safe Handling**Local Exhaust:  
General Ventilation:None should be needed.  
Recommended.

Dangerous Goods Class:

Not applicable.

**Dow Corning Australia Pty Ltd  
Material Safety Data Sheet****DOW CORNING 200(R) FLUID, FOODGRADE, 350 CST**

Handling Precautions: Use with adequate ventilation. Avoid eye contact. Do not take internally. Exercise good industrial hygiene practice. Wash after handling, especially before eating, drinking or smoking. If this product is heated to > 150 degrees C, trace quantities of formaldehyde may be released, and adequate ventilation is required

Storage Conditions: Use reasonable care and store away from oxidizing materials.

Unsuitable Packaging Materials: None established.

**5.2 Spills**

Personal Precautions: Avoid eye contact. Do not take internally.

Environmental Precautions: Prevent from spreading or entering into drains, ditches or rivers by using sand, earth or other appropriate barriers.

Methods for Cleaning up: Determine whether to evacuate or isolate the area according to your local emergency plan. Observe all personal protective equipment recommendations described in this MSDS. If diked material can be pumped, store recovered material in appropriate container. Clean up remaining materials from spill with suitable absorbant. Clean area as appropriate since some silicone materials, even in small quantities, may present a slip hazard. Final cleaning may require use of steam, solvents or detergents. Dispose of saturated absorbant or cleaning materials appropriately, since spontaneous heating may occur. Laws and regulations may apply to releases and disposal of this material, as well as those materials and items employed in the cleanup of releases. You will need to determine which laws and regulations are applicable.

**5.3 Waste Disposal**

Product Disposal: Dispose of in accordance with local regulations.

Packaging Disposal: Packaging should be disposed of in accordance with regional and/or national regulations.

**5.4 Stability and Reactivity**

Stability: Stable.

Conditions to Avoid: None.

Materials to Avoid: Oxidizing material can cause a reaction.

Hazardous Decomposition Products: Carbon oxides and traces of incompletely burned carbon compounds. Silicon dioxide. Formaldehyde.

Hazardous Polymerisation: Hazardous polymerization will not occur.

**5.5 Fire/Explosion Hazard**

Extinguishing Media: On large fires use dry chemical, foam or water spray. On small fires use carbon dioxide (CO<sub>2</sub>), dry chemical or water spray. Water can be used to cool fire exposed containers.

Unsuitable Extinguishing Media: None established.

Unusual Firefighting Hazards: None.

**Dow Corning Australia Pty Ltd  
Material Safety Data Sheet****DOW CORNING 200(R) FLUID, FOODGRADE, 350 CST**

Special Firefighting Procedures:	Self-contained breathing apparatus and protective clothing should be worn in fighting large fires involving chemicals. Determine the need to evacuate or isolate the area according to your local emergency plan.
Hazardous Decomposition Products:	Carbon oxides and traces of incompletely burned carbon compounds.
Hazchem Code:	Silicon dioxide. Formaldehyde. Not applicable.

**6. Regulatory Information****6.1 Classification and Labelling**

<b>Classification:</b>	Not hazardous.
<b>R-phrases:</b>	Not hazardous.
<b>S-phrases:</b>	S24/25 Avoid contact with skin and eyes.

**6.2 Chemical Inventories**

AICS:	All ingredients listed or exempt.
DSL:	All chemical substances in this material are included on or exempted from the DSL.
MITI:	All components are listed on ENCS or its exempt rule.
KECL:	All ingredients listed, exempt or notified.
EINECS:	All ingredients listed or exempt.
TSCA:	All chemical substances in this material are included on or exempted from listing on the TSCA Inventory of Chemical Substances.
PICCS:	All ingredients listed or exempt.
IECSC:	Not determined.

**7. Other Information**

Contact Point:	Technical Services Engineer 1300-360-732
Prepared by:	Dow Corning Australia Pty Ltd

This MSDS summarises our best knowledge of the health and safety hazard information of the product and how to safely handle and use the product in the workplace. Each user should read this MSDS and consider the information in the context of how the product will be handled and used in the workplace including in conjunction with other products. If clarification or further information is needed to ensure that an appropriate risk assessment can be made, the user should contact this Company. Our responsibility for products sold is subject to our standard terms and

**DOW CORNING**

Page: 6/6  
Last Revision Date 2001/10/29  
Version: 1.0

**Dow Corning Australia Pty Ltd  
Material Safety Data Sheet**

**DOW CORNING 200(R) FLUID, FOODGRADE, 350 CST**

conditions, a copy of which is sent to our customers and is also available on request.

**(R) indicates Registered Trademark**

**\*\*\*\*\* This is the last page. \*\*\*\*\***





24 Madison Road, Fairfield, New Jersey 07004, USA  
 Tel: 800-771-JEEN (5336), Tel: 973-439-1401, Fax: 973-439-1402,  
 email: [info@jeen.com](mailto:info@jeen.com) , Website: [www.jeen.com](http://www.jeen.com)

#### 4. FIRST AID MEASURES

Skin:	Immediately flush skin with plenty of water. Remove contaminated clothing and shoes. Call a physician if irritation develops and persists. Wash clothing before reuse. Thoroughly clean shoes before reuse.
Eyes:	Immediately flush eyes with plenty of water for at least 15 minutes. If easy to do, remove contact lenses, if worn. Get medical attention.
Inhalation:	Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.
Ingestion:	If large quantities of this material are swallowed, call a physician immediately. Do NOT induce vomiting unless directed to do so by a physician. Never give anything by mouth to an unconscious person. Get medical attention.

#### 5. FIRE FIGHTING MEASURES

**NFPA:**                      **Health: 1**                      **Flammability: 1**                      **Reactivity: 0**

Flammable properties Flash point (test method):	109 C (228 F) (Closed Cup)
Flammable limits in air, % by volume:	Upper: No Information    Lower: No Information
Autoignition temperature:	394 C (741 F)
Products of combustion:	Carbon monoxide and butadiene.
Extinguishing Media:	Use alcohol type aqueous film forming foam for large fires. Use CO <sub>2</sub> or dry chemical for small fires.
Fire Fighting Environmental Concerns:	Thoroughly decontaminate bunker gear and other fire-fighting equipment before re-use.
Fire Fighting Instructions:	Water spray should be used to cool fire-exposed structures and vessels. Water or foam may cause frothing. Water spray can be used to reduce the intensity of flames and to dilute spills to a non-flammable mixture. Keep personnel removed from and upwind of fire. If potential for exposure to vapors or products of combustion exists, wear full fire fighting turnout gear and NIOSH approved self-contained breathing apparatus. Oxidizing chemicals may accelerate the burning rate in a fire situation.

#### 6. ACCIDENTAL RELEASE MEASURES

##### SPILL OR LEAK INSTRUCTIONS

See Section 8 for appropriate personal protective equipment. Contain spill with dikes of soil or nonflammable absorbent to minimize contaminated area. Avoid run-off into storm sewers and ditches leading to waterways. If required, notify state and local authorities. Place leaking containers in well-ventilated area. Clean up small spills by using a nonflammable absorbent or flushing sparingly with water. Contain larger spills with nonflammable diking or absorbent. Clean up by vacuuming or sweeping.

Keep unnecessary people away; isolate hazard area and deny entry. Stay upwind; keep out of low areas. Assess the spill situation, as the spill may not involve large amounts of hazardous airborne contaminants in many outdoor spill situations. It may be advisable in some cases to simply monitor the situation until spilled product is removed.



24 Madison Road, Fairfield, New Jersey 07004, USA  
 Tel: 800-771-JEEN (5336), Tel: 973-439-1401, Fax: 973-439-1402,  
 email: [info@jeen.com](mailto:info@jeen.com) , Website: [www.jeen.com](http://www.jeen.com)

### 7. HANDLING AND STORAGE

**Handling:** Use with adequate ventilation. Keep containers closed when not in use. Always open containers slowly any excess pressure to vent. Avoid breathing vapor. Avoid open containers slowly to allow any excess pressure to vent. Avoid breathing vapor. Avoid contact with eyes, skin or clothing. Wash thoroughly with soap and water after handling. Decontaminate soiled clothing thoroughly before re-use. Destroy contaminated leather clothing.

This product may generate a static charge. Ground/bond equipment when transferring material to prevent static accumulation. Electrical equipment and circuits in all storage and handling must conform to requirements of National Electric code (Article 500 and 501) for hazardous location.

**Storage:** Do not store with incompatible materials. See Section 10. Stability and Reactivity.

### 8. EXPOSURE CONTROLS / PERSONAL PROTECTION

**Engineering Controls:** General or dilution ventilation is frequently insufficient as the sole means of controlling employee exposure. Local ventilation is usually preferred.

**Protective Equipment:** A safety shower and eyebath should be readily available.

**Skin Protection:** Wear impervious clothing and gloves to prevent contact. Nitrile rubber is recommended. Other protective material may be used, depending on the situation, if adequate degradation and permeation data is available. If other chemicals are used in conjunction with this chemical, material selection should be based on protection for all chemicals present.

**Eye/face Protection:** Wear chemical goggles when there is a reasonable chance of eye contact.

**Respiratory Protection:** Based on workplace contaminant level and working limits of the respirator, use a respirator approved by NIOSH. The following is the minimum recommended equipment for an occupational exposure level. To estimate an occupational exposure level see Section 3, Section 8 and Section 11.

For concentrations > 1 and < 10 times the occupational exposure level: Use air-purifying respirator with full face piece and organic vapor cartridge(s) or air-purifying full face piece respirator with an organic vapor canister or a full face piece powered air-purifying respirator fitted with organic vapor cartridge(s). The air purifying element must have an end of service life indicator, or a documented change out schedule must be established. Otherwise, use supplied air.

For concentrations more than 10 times the occupational exposure level and less than the lower of either 100 times the occupational exposure level or the IDLH: Use Type C full face piece supplied-air respirator operated in positive-pressure or continuous-flow mode.

For concentrations > 100 times the occupational exposure level or greater than the IDLH level or unknown concentrations (such as in emergencies): Use self-contained breathing apparatus with full face piece in positive-pressure mode or Type C positive-pressure full face piece supplied-air respirator with an auxiliary positive-pressure self-contained breathing apparatus escape system.

For escape: Use self-contained breathing apparatus with full face piece or any respirator specifically approved for escape.

#### EXPOSURE GUIDELINES

Component & CAS Number:	1,3-Butylene Glycol	107-88-0
Weight %:	99.5	
ACGIH TWA - ACGIH STEL -	ACGIH CEILING - OSHA TWA - OSHA STEL - OSHA CEILING -	
Component & CAS Number:	1,3 - Butylene Glycol	107-88-0
Weight %:	99.5	
1990 NIOSH IDLH (Recognized by OSHA) -	1994 NIOSH IDLH -	

**Comments:** No exposure guidelines have been established by ACGIH or OSHA.



hed by NIOSH

24 Madison Road, Fairfield, New Jersey 07004, USA  
Tel: 800-771-JEEN (5336), Tel: 973-439-1401, Fax: 973-439-1402,  
email: [info@jeen.com](mailto:info@jeen.com) , Website: [www.jeen.com](http://www.jeen.com)

#### 9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance:	Clear, colorless, mobile, syrupy liquid.
Odor:	Essentially odorless
Vapor Pressure:	0.06 mm Hg at 20 deg. C
Vapor density (Air=1 @ 20 deg. C):	3.2
Boiling Point (760 mm HgA):	207.5 C (405.5 F)
Freezing Point:	-50 C (-58 F)
Specific gravity:	1.0059 at 20 deg. C
Molecular weight:	90.12

#### 10. STABILITY AND REACTIVITY

Stability:	Stable
Incompatibility:	Keep away from sulfuric acid, phosphoric acid and other dehydrating agents, acetic anhydride, strong oxidizing agents such as peroxides, oxygen, nitric acid, perchloric acid or chromium trioxide.
Hazardous combustion or decomposition products:	Thermal decomposition products may include oxides of carbon. Thermal decomposition products may include oxides of carbon and butadiene.
Hazardous Polymerization:	Hazardous polymerization will not occur.

#### 11. TOXICOLOGICAL INFORMATION

Component & CAS Number:	1,3 Butylene Glycol 107-88-0
Weight %:	99.5
Component toxicological Information:	Acute Exposure:
Oral LD50:	18.6 – 30 g/kg (rats); practically nontoxic to animals
Inhalation LC50:	No mortality following 8 hour exposure to saturated vapor (concentration not specified).
Skin:	Minimally irritating to skin; no evidence of skin sensitization. Practically nontoxic to animals (estimated LD50, guinea pigs > 20 g/kg based on repeated exposure study).
Eyes:	No irritation to slight irritation in rabbit eyes, depending on the concentration administered.
Mutagenicity:	Not mutagenic in vivo (rat dominant lethal and cytogenetic assays). No in vitro information available.
Carcinogenicity:	No toxic effects in rats after administration of 1, 3, or 10% (approximately 1-12 g/kg/day) in the diet for up to two years.
Reproductive/Developmental Effects:	1,3-butylene glycol was administered at 5, 10, or 24% (approximately 2.5, 5 or 12 g/kg/day) in the diet to male and female rats over five generations. Reproduction and lactation parameters were comparative to controls for four or five generations of parents and offspring. The pregnancy rate of F1A rats decreased during five successive mating cycles. Excluding this group, the viability of F2 generation pups revealed no significant differences between litters or between control and test groups. In a teratology study conducted as part of the reproduction study, no definitive dose-related teratological findings in either soft or skeletal tissue were noted. Fetotoxicity (e.g., delayed ossification of sternebrae) was noted at the 10% and 24% doses. A dietary level of 20% (approx. 10 g/kg/day) produced no developmental effects in the three generation study despite reduced parental weight gain. In a teratology study, rats administered 0.7, 4.2 or 7.1 g/kg/day orally by gavage on days 6-15 of gestation showed sedation at the two higher doses; a dose-related reduction in the average bodyweight of offspring was found. No teratogenic effects were noted.



24 Madison Road, Fairfield, New Jersey 07004, USA  
Tel: 800-771-JEEN (5336), Tel: 973-439-1401, Fax: 973-439-1402,  
email: [info@jeen.com](mailto:info@jeen.com) , Website: [www.jeen.com](http://www.jeen.com)

#### 11. TOXICOLOGICAL INFORMATION continued...

Repeated Exposure: Rats exposed to doses of 1-10% in the diet (approximately 1-12 g/kg/day) for two years of 5-40% in the diet (3.4-22.5 g/kg/day) for eight weeks showed no evidence of toxic effects. Dogs exposed orally to doses up to 1 g/kg/day showed no evidence of toxic effects. No adverse effects were observed when undiluted 1,3-butylene glycol was applied for 2 hr/day to the intact or abraded skin of guinea pigs for 4 or 14 days respectively, at a dose of 20 g/kg/day. Numerous studies have been conducted to investigate the effect of substituting 1,3-butylene glycol in place of carbohydrate in the diet of various species of animals, including rats, dogs, pigs and cows. Up to a dietary level of about 1-15%, this chemical appears to be well utilized as a source of energy, but at higher levels growth is impaired.

#### 12. ECOLOGICAL INFORMATION

Component & CAS Number: 1,3-Butylene Glycol 107-88-0  
Weight %: 99.5

##### Component Ecological Information:

Ecotoxicity: 1,3-Butylene Glycol is estimated to have low acute toxicity to aquatic species.

Fish, OSAR-Estimated 96-hr. LC50 using Computer Program (EPA ECOWIN v 0.99E.ECOSAR software): 9514 mg/l.

Crustacean (Daphnia), OSAR-Estimated 48-hr. LC50 using Computer Program (EPA ECOWIN v 0.99E.ECOSAR software): 8703 mg/l

Algae, Green (Selenastrum capricornutum: OECD 201) 72-hr. EC50: > 1070 mg/l (measured concentration). Neither the area under the growth nor the growth rate were reduced by 1,3-butylene glycol at a mean measured level of 1070 mg/l. Therefore, the "no-observed effect concentration" for algal growth inhibition was greater than or equal to 1070 mg/l.

Bacteria (Activated Sludge-Respiration Inhibition test; OECD 209) 3-hr. EC50: > 100mg/l (nominal conc.). No inhibitory effect on the respiration of activated sludge at 100 mg/l or the other lower concentrations tested.

##### Environmental Fate:

Degradation: Ready biodegradability was assessed in the Carbon Dioxide Evolution Test (Modified Sturm Test; OECD 301b). 1,3-Butylene glycol met the criteria for "ready biodegradability". Degradation progressed throughout the test period as follows: 10% degradation after 3 days; 60% after 12 days; 81% degradation by the end of the test on Day 29. Atmospheric photodegradation half-life was calculated to be 9.0 hours.

Bioaccumulation: The calculated log n-octanol/water partition coefficient is -0.2909. This indicates low potential for bioaccumulation.

#### 13. DISPOSAL CONSIDERATIONS

Dispose of spilled material in accordance with state and local regulations for waste that is non-hazardous by Federal definition. Note that this information applies to the material as manufactured; processing, use, or contamination may make this information inappropriate, inaccurate, or incomplete.

Note that this handling and disposal information may also apply to empty containers, liners and rinsate. State or local regulations or restrictions are complex and may differ from federal regulations. This information is intended as an aid to proper handling and disposal; the final responsibility for handling and disposal is with the owner of the waste. See Section 9 – Physical and Chemical Properties.



24 Madison Road, Fairfield, New Jersey 07004, USA  
Tel: 800-771-JEEN (5336), Tel: 973-439-1401, Fax: 973-439-1402,  
email: [info@jeen.com](mailto:info@jeen.com) , Website: [www.jeen.com](http://www.jeen.com)

#### 14. TRANSPORT INFORMATION

##### US DEPARTMENT OF TRANSPORTATION

Shipping Name: 1,3-Butylene Glycol  
Hazard Class: Not regulated

##### ICAO/IATA:

Proper Shipping Name: 1,3-Butylene Glycol  
Hazard Classification: Not Regulated

##### IMDG:

Proper Shipping Name: 1,3-Butylene Glycol  
Hazard Class: Not Regulated  
Flash Point (test method): 109 C (228F) (Closed Cup)

**Transport Canada** PRODUCT IS NOT REGULATED IAW TDG REGULATIONS

Proper Shipping Name:  
Trade Information

Schedule B Code (export): 2905.39.1000

#### 15. REGULATORY INFORMATION

##### U.S. FEDERAL REGULATIONS

Chemicals associated with the product which are subject to the state right-to-know regulations are listed along with the applicable state(s).

##### U.S. REGULATORY RULES

TSCA Inventory: We certify that all components are either on the TSCA inventory or qualify for an exemption.

##### ENVIRONMENTAL REGULATIONS

##### SARA 311:

Acute Health: Yes  
Chronic Health: No  
Fire: No  
Sudden release of pressure: No  
Reactive: No

##### INTERNATIONAL REGULATIONS

AUSTRALIA – CANADA – EUROPE – KOREA – PHILIPPINES

##### CANADIAN REGULATIONS:

WHMIS Classifications: Not a WHMIS controlled product.

#### 16. OTHER INFORMATION

Hazard Ratings: This information is intended solely for the use of individuals trained in the NFPA and/or HMIS systems.

**NFPA:** HEALTH – 1  
FLAMMABILITY – 1  
REACTIVITY – 0

**HMIS:** HEALTH – 1  
FLAMMABILITY – 1  
REACTIVITY – 0

**NOTE:** For industrial use only.

The information contained herein is accurate to the best of our knowledge. We do not suggest or guarantee that any hazards listed herein are the only ones which exist. JEEN International makes no warranty of any kind, express or implied, concerning the safe use of this material in your process or in combination with other substances. Effects can be aggravated by other materials and/or this material may aggravate or add to the effects of other materials. This material may be released from gas, liquid, or solid materials made directly or indirectly from it. User has the sole responsibility to determine the suitability of the materials for any use and the manner of use contemplated. User must meet all applicable safety and health standards.



Design of a sunscreen plant and the rheological study of the emulsion by [Corbí García, Paula](#) is licensed under a [Creative Commons Reconocimiento-NoComercial-SinObrasDerivadas 4.0 Internacional License](#).

Puede hallar permisos más allá de los concedidos con esta licencia en <http://creativecommons.org/licenses/by-nc-nd/4.0/deed.ca>