Improving the effectiveness of Coagulation and Separation of rubber from skim from centrifuging of field latex

By

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DECLERATION

The research work described in this thesis was carried out at Dipped Products Limited under the supervision of Dr.L.P. Nethsinghe and Prof. D.B.M. Wickramaratne.

A report on this has not been submitted to another university for another degree.

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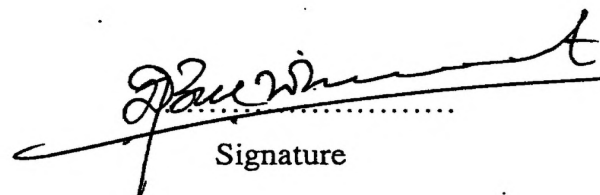**Certified by**

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DEDICATED TO MY PARENTS

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Abstract

Natural rubber is extracted from the bark of the trunk of *Hevea brasiliensis* tree by a process called tapping. Field latex is centrifuged to concentrate its DRC (Dry Rubber Content) depending on the purpose. This process results skim latex as a byproduct which has 3 -7% DRC. Incomplete coagulation of skim latex results environmental problems when it is discharged to the environment and hence expence high value to treat effluent. The current skim processing involves the recovery of 4-5% of rubber content by cheap grade sulphuric acid coagulation. By using proper acid dosage, maximum rubber yield can be recovered reducing effluent problems.

In the assessment, skim is treated with sulphuric and formic acids and then with different concentrations, until maximum yield of rubber is obtained. Also papain, protein digesting enzyme, is used as alternative coagulant after neutralizing skim with sulphuric acid. The coagulation of latex by the addition of acids is a result of the precipitation of the protective layer of proteins around the rubber globules in the latex by lowering of pH.

As a result of series of trials, 25% formic acid and 98% sulphuric acid recover higher yield than others. To coagulate 100 L of skim, only 1kg and 2kg of sulphuric acid and formic acid are enough respectively. 98% sulphuric acid yields recovery of 98% rubber while formic acid yields 97%. In neutral state of skim, very low quantity of papain is enough to coagulate than in normal state due to its enzymatic activity. Extracted protein levels of dried products were varied from the expected results. However coagulation with alum separate rubber, but can not get separated as it come as a suspension.

The DRC value after 14 hours was further reduced when drying duration was lengthen up to 18 hours. Then the latter was used during the result calculation. The recovered yield of rubber becomes increasing with increasing the concentration of sulphuric acid and *vice versa*, but not other coagulating agents.

Content

Chapter 3 - Materials and Methodology

Abbreviation

BOD ; Biological Oxygen Demand

^0C ; Centigrade

CL ; Centrifuged Latex

COD ; Chemical Oxygen Demand

DPL ; Dipped Products Limited

DRC ; Dry Rubber Content

EP ; Extracted protein

et al. ; And others

FAS ; Ferrous Ammonium Sulphate

FL ; Field Latex

g ; Grammes

kg ; Kilo gramme

L ; Litre

μ ; Micro

m ; Meter

mg ; Mili grammes

ml ; Mili litre

mm ; Mili meter

mol ; Moles

MST ; Mechanical Stability Test

nm ; Nanometer

NR ; Natural rubber

ppm ; Parts per million

rpm ; Rounds Per Minute

ton ; Tonnes

TSC ; Total Solid Content

TSS ; Total Suspended Solids

VFA ; Volatile Fatty Acids

List of figures

List of tables

CHAPTER 1

Introduction

1.1 Background of industry

1.1.1 Dipped Products Limited (DPL)

Dipped Products Limited is one of members of Hayleys group which supplies gloves to global market mainly. It incorporated 1976 and became to a leading glove manufacturing company. As hand protection and plantations, there are two major aspects of company. Dipped Products, Grossart, Venigros, Neoprex, Texnil, Dipped Products(Thailand) and Hanwella Rubber Products are manufacturing companies of hand protection.

DPL has compounding, production, quality assurance, finishing and effluent treatment sections based on their processes.

1.1.2 Products and competition

Today DPL services up to 5 percent of global demand – placing them within the top 5 glove manufacturers in the world. (http://www.dplgroup.com/globalreach.html) House hold(Nitrile) glove, supporter glove, surgical glove are produced in DPL.

1.1.3 Quality Assurance

For high quality products, quality assurance is done by Quality Assurance lab. Initially latex is tested before purchasing based on their purposes and approved or not depending on their result. Purchased latex is used to compounding and again for testing. There are few tests which are done to test the quality of the latex.

1.1.3.1 Dry Rubber Content (DRC) Test

It determines DRC of Field Latex (FL), Centrifuged Latex (CL) or skim sample. Based on DRC value, it can be suggested that as natural, diluted or a spoiled sample.

1.1.3.2 Total Solid Content (TSC) Test

It tests for TSC in latex sample. If TSC is higher, DRC is automatically higher. DPL has standard level to pass the FL to get in. The relation between TSC and DRC as follows.

$$TSC = DRC + 2\% \ Max$$

1.1.3.3 Mechanical Stability Test (MST)

Mechanical Stability Test is done to measure the stable time duration of latex without coagulating on mechanical force. Here, the latex undergoes high speed rotation (14000 rpm) and its coagulation initiation time is checked.

1.1.3.4 Volatile Fatty Acid (VFA) Test

The good or bad conditioned latex is identified by Volatile Fatty Acid test. Sample is subjected to a series of tests and finally titrated with barium hydroxide $(Ba(OH)_2)$. Less titrant volumes are accepted or otherwise rejected.

1.1.3.5 KOH Test

Non volatile fatty acids in FL are tested using this test. If ammonia content is high, formaldehyde is added.

1.1.3.6 NH₃ Test

To prevent the microbial action, ammonia is added. Also ammonia content is checked weekly to test the content.

1.1.3.7 Chemical Oxygen Demand (COD) Test

The COD is another index of pollution which measures the effect of pollutants on dissolved oxygen. In the COD test, an oxidant instead of oxygen is used to degrade the pollutants in the water sample. It is a useful measure of water quality and expressed in milligrams per liter (mg/L).

All organic compounds of the sample are fully oxidized into carbon dioxide with a strong oxidizing agent in the presence of acid in this test. Also ammonia converts to nitrate in this process.

$$NH_3 + 2O_2 \longrightarrow NO_3^- + H_3O^+$$
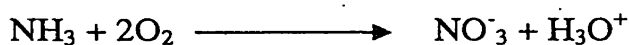
Under acidic condition, potassium dichromate reacts with organic compounds like below.

$$C_nH_aO_bN_c + dCr_2O_7^{-2} + (8d+c)H^+ \longrightarrow nCO_2 + \frac{(a+8d-3c)}{2} H_2O + cNH_4^+ + 2dCr^{+3}$$
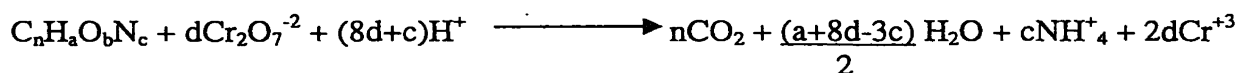
Dichromate is reduced in to $Cr+^3$ by the organic compounds in the sample. Because COD measures the oxygen demand of organic compounds in a sample of water, it is important that no outside organic material be accidentally added to the sample to be measured. To control this, a so-called blank sample is required in the determination of COD. For all organic matter to be completely oxidized, an excess amount of potassium dichromate is added. After completing the oxidation, the amount of excess potassium dichromate can be

measured to ensure that the amount of Cr^{3+} can be determined with accuracy. The excess potassium dichromate is titrated with FAS until all the excess oxidizing agent has been reduced to Cr^{3+}. The oxidation-reduction indicator, ferroin, is added during this titration. Once all the excess dichromate has been reduced, the ferroin indicator changes from blue-green to reddish-brown. The amount of ferrous ammonium sulfate added is equivalent to the amount of excess potassium dichromate added to the original sample.

The change in colour corresponds to the formation of the complex ferrous phenantroline which occurs when all dichromate ions have been reduced to Cr^{3+}:

$$(Fe(C_{12}H_8N_2)_3)^{+3} + e \longrightarrow (Fe(C_{12}H_8N_2)_3)^{+2}$$
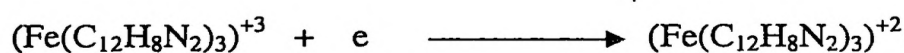
Ferric Phenanthroline (blue – green)   Ferrous Phenanthroline(reddish brown)

By using potassium dichromate as the oxidizing agent, wide variety of organic substances can be oxidized. Reflux condenser prevents the loss of volatile organics. Also same sensitivity is kept through out the experiment.

Ferroin is the chemical compound with the formula [Fe(o-phen)$_3$]SO$_4$, where o-phen is an abbreviation for 1,10-phenanthroline.

Source: (http://en.wikipedia.org/wiki/Ferroin)
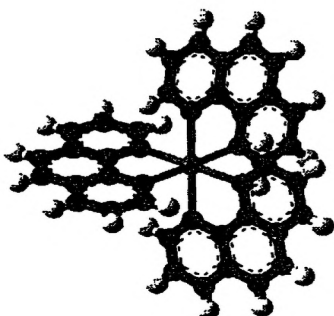
Figure 1.1 : [Fe(o-phen)$_3$]$^{2+}$ complex cation in ferroin

1.2 Problem Background

Skim is mainly composed with tiny rubber particles suspended in liquid which is chiefly water. Due to its low value of DRC, 3-7%, it is difficult to coagulate. If it is discarded to environment as its normal state, it damages soil and nature. Treatment of skim becomes a more complex process due to this polymeric substances and highly costive. Proper, exact acid dosage should be proposed to obtain higher yield with maximum coagulation.

3

Excess acid causes to acidic effluent resulting environmental problems, also dissolves the rubber protein and hence delay the coagulation process. Once skim rubber is recovered, the effluent consists of sulphuric acid contaminated serum with a high Biological Oxygen Demand (BOD) discharged in to the effluent ponds. Aerobic and anaerobic ponds situated next to the concentrate factory take the bulk of the effluent discharge from the processing activities. Microbial breakdown makes place below the scum layer in the anaerobic ponds, whereby the sulphate ions from sulphuric acid are converted to poisonous hydrogen sulphide gas. This pungent acidic gas is released once the scum layer is disturbed due to heavy downpour, thus affecting the environment of the surrounding area and leading to a chain of unpleasant events such as malodour and ill health of the surrounding residents.

By improving the separation and effectiveness of rubber from skim latex, it increases the profit and prevent discharge of effluent to environment. It inhibits the releasing of malodour and safe the health condition.

1.3 Objectives

1.3.1 Overall objective

Improving the effectiveness of Coagulation and Separation of rubber from skim from centrifuging of field latex.

1.3.2 Specific objectives

- Study the rubber processing method and quality parameters of field latex.
- Determine the best conditions to obtain maximum yield of rubber.
- Selecting the most feasible method to obtain high quality finished product of rubber.
- Find the user friendly method to separate the rubber after the treatment.

4

CHAPTER 2

Literature Review

2.1 History of rubber

Christopher Columbus brought an exudates sample from the tree *Hevea brasiliensis* from South America to Spain in 1498 (Gopalan *et al.*, 2000). The native land of *hevea* tree is considered as Amazon rain forests in South America. Rubber is a water proof material because it consist of a tangle of hydrocarbon chains that have no affinity for water (Bruice, 2003). It was first noted by Pizarro in 1540, but the Spaniards did not bring the process to Europe (Chandra, Adab, 1998). Sir Joshaph Hooker took rubber seeds to Britain from South America in 1873 as first step. By the end of eighteenth century, all properties of rubber were known by Europeans.

However first rubber plant was planted in Sri Lanka at Senarathgoda garden, Gampaha at 9th of August 1876 (Yapa, 1992). Now rubber industry is distributed through out all over the world due to its versatility.

2.2 Natural Rubber

2.2.1 *Hevea brasiliensis*

Family   : Euphorbiaceae

Genus   : Hevea

Species : brasiliensis

Common Names: Rubbertree, jebe, arbre de para, parakautschukbaum, cauchotero
de pará, seringueira, seringueira-branca, arbol del caucho, siringa

Synonyms: Siphonia brasiliensis Willd. ex A. Juss.

Part used : Leaves, bark, latex

Source: (http://www.rain-tree.com/rubber.htm)

Natural rubber is made from the milky fluid, called latex, obtained by cutting narrow strips from the bark of the rubber tree, *Hevea brasiliensis* (Bahadur *et al.*, 2005). Latex exudes through cut strips and collected to coconut shells. It is ammoniated to prevent bacterial attack and coagulation (NIIR Board, 1996).

The rubber particles are the more typical latex component. From 60nm to 6μm in diameter and up to 50% of the latex by weight, these particles are wrapped in a mono membrane made of negatively-charged glycolipo-phosphoproteins. The negative charges allow stability of the latex colloidal suspension (Auzac, 2007). The contribution of negative

5

charges from the adsorbed proteins towards the stability of the latex is of less importance (Ho ,1989).

Figure 2.1: Latex exudates

Among the proteins located in the membrane rubber particles, two enzymes implicated in the elongation of the cis-polyisoprene chain have been found. The cis-prenyl transferase (76Kd) and the Rubber Elongation Factor (REF, 14.6Kd), and also a glycoprotein (22Kd) which is implicated in latex coagulation by its glucidic moiety(Auzac, 2007).

2.2.2 Colloidal stability of natural rubber particle

The main forces which influence on the NR particle motion are Drag force, Buoyancy force, Brownian force, Surface Tension force, screened electrostatic repulsions, steric repulsions and Van der Waals attractions.

In colloidal systems, a drag force arises due to the resistance of surrounding fluid to the motion of particles. The resistance is caused by the viscous shear of the fluid flowing over the particles and by the pressure difference between the upstream and downstream sides of the moving particle in the colloidal system. The drag force acts in a direction opposite to particle velocity, thus opposing the particle motion. The magnitude of the drag force is dependent on viscosity of the surrounding fluid, particle size and its velocity. The drag force has a higher magnitude for a fluid with higher viscosity and for larger particles. As particle velocity increases, the resistance to motion increases linearly resulting in higher magnitude of drag force.

A buoyancy force arises due to the density difference between the particles and the suspending fluid in colloidal systems. Based on whether the density of particle is lesser or greater than the suspending fluid, the buoyancy force acts either in vertically upward direction or in vertically downward direction respectively.

Colloidal particles, which are in the size range of 100 nm to 1000 nm, are under constant Brownian motion. This arises due to the thermal energy associated with the suspending fluid. The thermal energy of the fluid molecules causes them to undergo collisions with suspended particles, thereby resulting in random-walk motion.

In colloidal systems, the surface tension force acting on particles at air-water interface has the effect of trapping the particles within the liquid. When particles reach the air-water interface, force due to surface tension dominates over all other forces causing the particles to move along with the interface. Surface tension force arises due to anisotropic attractive forces existing between molecules at the interface. The attractive forces existing between molecules away from the interface are isotropic because of the molecules surrounding them in all directions. But molecules at the interface do not have any molecules above them, resulting in higher transverse attractive forces and thereby causing anisotropy in attractive forces.

As latex dispersions are lyophobic in nature, the surface charge provides only kinetic stability and not thermodynamic stability. Given enough time, they finally form an aggregate. The electrostatic repulsions between the particles create an energy barrier that prevents immediate coagulation. The magnitude of the energy barrier can be controlled by varying the surface charge and also the electrolyte concentration. The higher the electrolyte concentration, the lower is the magnitude of the energy barrier.

Thus, the electrostatic interaction between charged colloidal particles involves not only the interactions between the colloidal particles, but also the interactions between colloidal particles and the sea of ions surrounding the particles. These ions may be counter ions or co ions or ions due to an added electrolyte. The colloidal particles are called macro ions and other ions are called simple ions. Macro ions influence the distribution of simple ions, which in turn influence the interaction between colloidal particles resulting in screened repulsions.

Despite these complications, Deryagin, Landau, Verwey and Overbeek (1942) proposed a useful theory to account for the interactions between colloidal particles. This theory has its own limitations due its assumptions. The theory has been widely accepted and is used in the present model to predict electrostatic interactions between latex particles. As every particle has a finite surface charge, there should be an excess of ions of opposite charge in the solution to maintain overall electric neutrality of the system. The ions present in the solution are not uniformly distributed in the solution. The oppositely charged ions are attracted towards the ions present on the surface of particles. But the thermal motion of the ions counteracts this electrostatic attraction. Thus, the ions take an equilibrium position to balance the electrostatic interaction energy with the thermal energy. This results in a diffuse double layer of ions surrounding the particle, one layer formed from the charge on the surface

of the particles and the other layer formed from the excess of oppositely charged ions present in the solution. Concentration of oppositely charged ions decreases as distance from the particle increases.

Vander Waals attractive forces are weak forces that exist between uncharged molecules as a result of induced polarity. These forces become significant when the particles are very smaller in size and when the distances are in the nano level. The origin of Vander Waals attractions may be related to the fluctuations in the charge distribution of atoms. As the electron cloud in an atom is in continuous motion, there are moments when the electrons are crowded at one side giving temporary polarity to the atom. This induces temporary polarity to the adjacent atom by repelling the electron cloud. According to that, the attractive forces between atoms are additive in nature. Because of this nature, the attractive interaction between two colloidal particles containing many atoms is appreciable, despite the force between two atoms being weak. The Vander Waals attractive forces between atoms are very short ranged, evident from the fact that they decrease with the seventh power of inter particle distance. Because of their additive nature, attractive forces between colloidal particles decrease much more slowly (Gundabala, 2002).

2.2.3   Composition

Table 2.1 : Composition of latex

Constituents	Percentage
Water	55...70
Rubber	30...40
Resins	1.5...2
Protein	1.5...3
Ash	0.5...1
Sugar	1...2

Source:(http://www.tisgdv.de/tis_e/ware/kautschuk/naturkautschuk/naturkautschuk.ht m#informationen)

The isoprene units of natural rubber are all linked in head to tail fashion and all of the double bonds are cis (Solomons, 1995). *Hevea* rubber contains 93-95% weight of cis isomer (Bhatnagar, 2004). Gutta percha is trans form of polyisoprene. On coagulation and evaporation to dryness, it gives a solid substances containing approximately 95% polyisoprene, the rest being water and non rubbery substances such as proteins, sterols, sugar and minerals (Bahadur *et al.*, 2005)

Depending on the clone, seasonal effects, and the state of the soil, the average composition of latex is as follows. 25 to 35% (wt/wt) polyisoprene, 1 to 1.8%

(wt/wt) protein, 1 to 2% (wt/wt) carbohydrates, 0.4 to 1.1% (wt/wt) neutral lipids, 0.5 to 0.6% (wt/wt) polar lipids, 0.4 to 0.6% (wt/wt) inorganic components, 0.4% (wt/wt) amino acids, amides, etc., and 50 to 70% (wt/wt) water(Rose, Steinbuchel, 2005).

2.2.3.1 Elasticity of rubber

Isoprene molecules polymerize together resulting randomly coiled linear polymer and this can be stretched and compressed like a spring. During stretching, macromolecules partially align with respect to another which causes to crystallization and stiffen the material. When stress is released, polymer chains revert back to its original coiled state end results amorphous product.

2.2.3.2 Polymerization

Natural rubber is a cis-1,4polyisoprene and has the structural formula $CH_2=CMe-CH=CH_2$ (Bhatnagar, 2004). During the treatment, these isoprene molecules polymerize to form long coiled chains of polyisoprene.
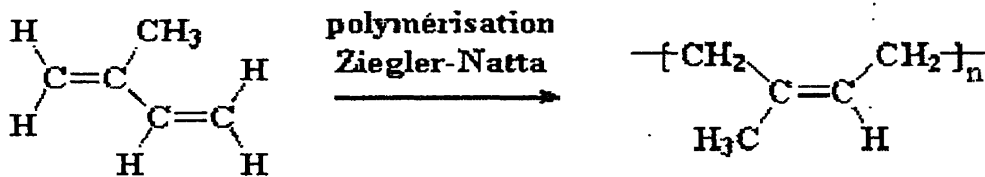
Figure 2.2: Ziegler Natta polymerization

2.2.4 Anatomy

The tree grows up to about 30m tall, tap root 4.5m and side roots about 7-10m long. The trifoliate leaves are formed in flushes, particularly on young trees. In each flush, the first four to six leaves are large, with long petioles, and are separated by long internodes, while the internodes very stunted in the subsequent smaller leaves (Sigmund, Gustav, 1991).

2.2.5 Breeding

Hevea is cultivated plant. Improved cultivation methods lead to have higher yield. The propagation of new cultivars by vegetative method and cloning is relatively quick. General selection criteria is quick growth of the trunk, thick and smooth bark, good bark renewal after tapping, amount and the quality of the latex and resistance to wind damage.

2.2.6 Ecophysiology

The cultivation of *hevea* tree is limited to equatorial region, because it is a tropical rainforest tree. Optimal conditions of rain and temperature are 2000-4000mm and 28°C respectively.

It sheds all leaves in dry season and has ability to tolerate warm weather. It causes to reduce latex yield in this season.

2.2.7 Tapping and Processing

The tree can be tapped after 5 – 6 years. Special knife is used to tap the tree. The bark is cut as deeply as possible, but should be careful to safe the cambium. Otherwise it may affect the age of the tree and tapping difficulties (Macmillan, 1935). Latex flows to coconut shells immediately after tapping and allowed few hours. Due to enzymic and oxidative reactions, the latex coagulates in transit from field to factory sites. Required amount of ammonia, sodium sulphide, formaldehyde or boric acid is added as preservative (Bhatnagar, 2004).

As normal procedure, latex is diluted and adds acid to lower the pH. As a result of that, latex globules coagulate. The densities of NR and serum are 0.91 and 1.02 respectively and hence coagulum floats on surface.

Three methods are used to concentrate the rubber content as evaporation, creaming and centrifuging. Latter is more important and used in DPL.

FL is centrifuged using eight machines and CL is collected to specific tanks while remain is released to separate tanks. According the operation, double CL is made too. Normally CL has 60% of DRC and remain serum has 3-7%. This portion is transferred to out and coagulation is done.

There are eight basic natural rubber types which are recognized by appearance and description only. Those are;

1. Ribbed Smoked Sheets
2. Pale crepes
3. Estate brown crepes
4. Compo crepes
5. Thin brown crepes (Remills)
6. Thin brown crepes (Ambers)
7. Flat bark crepes
8. Pure smoked blanket crepes

(NIIR Board, 1996)

Charles Goodyear discovered that thermally stable rubber could be prepared by heating it with sulphur, called vulcanization in 1839. It is a process in which rubber is transformed from its plastic condition in to an elastic state by improving the degree of cross linking between chains in it (Gopalan *et al.*, 2000).

Table 2.2: Vulcanized rubber Vs raw rubber

Property	Raw rubber	Vulcanite
Tensile strength	200kg/cm^2	200kg/cm^2
Per cent elongation at break	1200	800
Retraction	Good	Very good
Water absorption tendency	Very high	Small
Chemical resistance	Poor	Good
Elasticity	Very high	Very low(Depend on Vulcanization)
Useful temperature range	10 – 60 ^{0}C	-40 – 100 ^{0}C
Tackiness	Marked	Slight
Resistance to organic solvents	Infinite(Soluble)	Large, but limited
Manipulability to desired shape	Not easy	Easy

Source: (Gopalan *et al.*, 2000)

A number of synthetic rubbers are produced by diene polymerization. Chloroprene (2-chloro-1,3-butadiene)is polymerized commercially to yield neoprene, an excellent rubber with weather resistance(Karunaratne, 1999).

2.2.8 Uses

The different applications of rubber for different use of purposes demand varying degrees of cross linking among the chains. About 50% of all rubbers go in to tire production, 25% for other vehicular applications and the rest goes in to other items such as surgical gloves and thin walled articles (Bahadur, Sastry, 2005). Threads, belting, condoms, battery containers are few products of rubber.

2.3 Synthetic rubber

With rapid industrialization, requirements of people were increased. Highly sophisticated rubber products were demanded and could not supply as necessary due to lack of production of rubber. Then synthetic rubber was produced improving its existing qualities.

The first synthetic rubber was styrene-butadiene rubber was originally developed in the United State of America during the second world war as a substitute for NR (Gopalan *et al*, 2000). This synthetic rubber has improved characteristics resistance, resistance to solvents and so on.

2.3.1 Styrene rubber (SBR)

Styrene rubber is produced by addition copolymerization of styrene and butadiene monomers in either an emulsion or a solution polymerization process (NIIR Board, 1996).

It has high abrasion resistance and high load bearing capacity. SBR is used to prepare motor tires, floor tiles, soles for shoes, footwear components, gaskets, adhesives and tank lining (Gopalan *et al.*, 2000).

Source:(http://www.eng.ku.ac.th/~mat/MatDB/MatDB/SOURCE/Struc/polymers/synrub/synr ub.htm)

Polystyrene   Polybutadiene
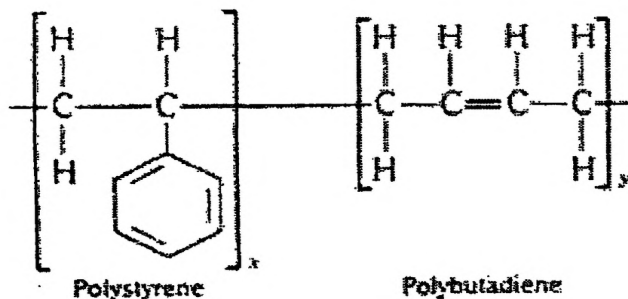
Figure 2.3: Basic structure of SBR

2.3.2 Nitrile rubber / Acrylonitrile rubber (NBR)

Nitrile rubber is copolymer of acrylonitrile and butadiene. The important characteristics of NBR are excellent oil resistance, solvent resistance and fuel oil resistance. NBR is used in oil resistance boxes, petroleum industrial parts, rubber rolls for printing, sealing material, o-rings, oil resistance soles, etc.(Chandra, Adab, 1998).

2.3.3 Polychloroprene (Neoprene) Rubber

Neoprene rubber production was based on the researches of the Father Nieuwland, who found (1921-1923) that vinyl acetylene combined with hydrochloric acid to yield 2-chloro-1,3-utadiene to which the name chloroprene was given(Chandra, Adab, 1998). Hoses, gaskets, tubes for carrying corrosive gases, sponges, adhesives are main products.

Source: (http://chemed.chem.purdue.edu/genchem/topicreview/bp/1polymer/terms.html)

$$n\ CH_2=CCH=CH_2 \longrightarrow [..(CH_2C=CHCH_2)_n..]$$

Chloroprene   Neoprene
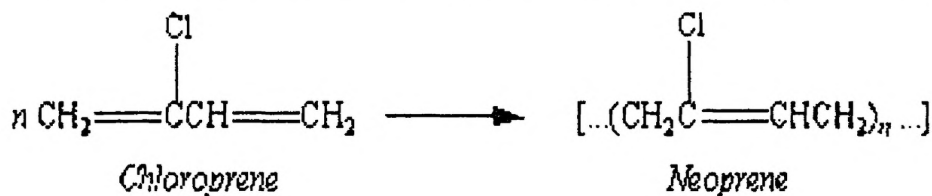
Figure 2.4: Neoprene formation

2.3.4 Silicone rubber (Silicones)

Silicone rubber shows exceptional qualities like resistance to weathering, common oils, boiling water, dilute acids, alkalis and ability to expose to sunlight. Silicone rubber has great thermal stability in between -80 to 250 °C with very little change in chemically and electrically (Chandra, Adab, 1998). Tires of air crafts, sealing material in searchlights, for insulating the electrical wiring in ships, as adhesives in electronic industry for making artificial valves, transfusion tubing and an implant surgery are few applications.

Source: (http://chemed.chem.purdue.edu/genchem/topicreview/bp/1polymer/terms.html)
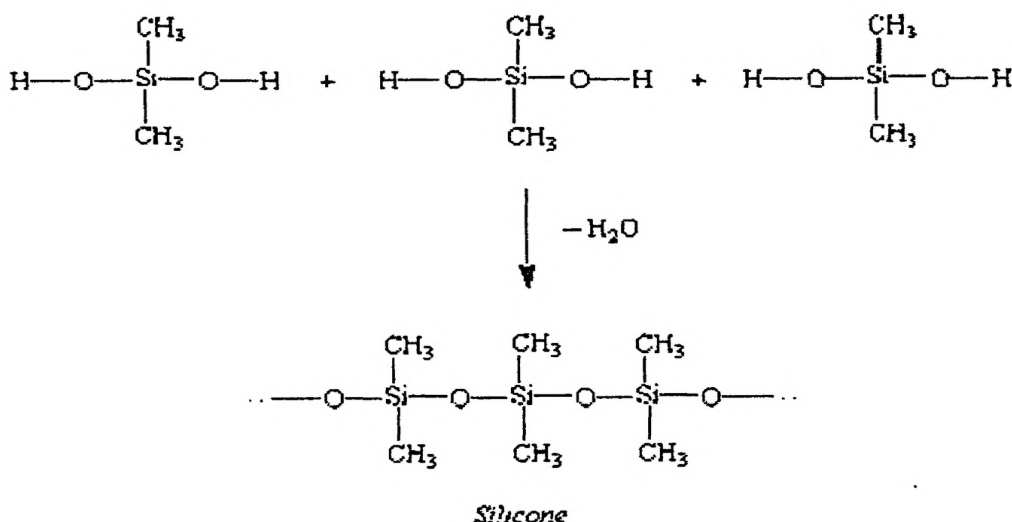
Figure 2.5: Silicone rubber polymerization

13

2.4 Skim

Skim latex is the by product of latex centrifuging process. If skim is deammoniated before coagulation, acid requirement can be reduced and the ammonia concentration in effluent may also be reduced (http://www.cpcb.nic.in/pciiiidivrubber.htm). It has a low DRC varying from 3-7% according to centrifuging and contains an abnormally high proportion of non rubber constituents such as fatty acids, proteins, sugars and inorganic salts (Pieris, 1970). Due to high content of non rubbery substances, it is considered as low quality rubber. However it is used to prepare hard goods such as belts in rice milling machines (Yapa, 1992).

In DPL, skim is transferred to Ukwelkanda Company and prepared rubber sheets are received back. Normally coagulation of skim is done by sulphuric acid. But incomplete coagulation leads to escape tiny rubber particles to effluent with skim serum.

2.4.1 Centrifugation

Since natural latex is a solution grouped in the colloidal system, it consists of rubber particles, suspended and dispersed in the serum. These rubber particles move about in a "brownian" motion. They are lighter than the serum, due to that the rubber particles tend to float to the latex surface. Rate of movement of rubber particles depends on the earth's gravity. By increasing the gravitational force, the speed of the rubber particles' movement will increase also. Therefore, centrifugation, which can increase gravitational force up to 2,000 – 3,000 times the earth's gravity, will lead to speed up the movement of the rubber particles. With this principle, a centrifuge was designed and created for producing concentrated latex for separating the rubber content from the serum.

As for skim latex, there is still some rubber content left remaining, which would be a shame to discard. Rubber content in the skim latex is no more than 8%, depending on the efficiency and setting of the centrifuge.

Concentrated latex produced will be preserved according to customer's demand.

2.4.2 Skim composition

Table 2.3: Chemical composition of skim

Constituent	Content %
Hydrocarbon	75 - 85
Rubber	5 - 8
Protein	9 - 18

Source: (Yapa, 1992)

14

Proteins are naturally occurring in natural rubber. These which can be present on the surface gloves, have been related to hypersensitivity reactions in some humans who come into contact with their skim. These same proteins also help to maintain the latex colloidal stability during collection and transport prior to manufacture. Consequently, when measures are taken to remove or degrade these proteins, other problems can be introduced, such as destabilization of the latex and changes in its coagulation properties.

2.4.3 Previous studies

Due to arised problems regarding with skim latex which is discarded to effluent, several experiments were done to reduce that. By recovering maximum yield of rubber from skim latex, DRC content in serum is reduced and hence effluent treatment problems are solved.

Ultra filtration is an alternative method of recovering rubber by skim latex, done by Rubber Research Institute of Malaysia. This method involves concentrating the skim latex by ultra filtration from DRC of 5% to 30% which is equivalent to the DRC of the field latex and subsequently adding it in to the incoming field latex for the continued production of latex concentration by centrifugation (Veerasamy, Aziz, 2007).

This process results serum without any rubber particles and also milky appearance. The natural rubber serum contains useful biochemicals. The single largest component of latex serum is water soluble carbohydrate. Quebrachitol which is a chemical feedstock for the synthesis of a range of bioactive materials(Veerasamy, Aziz, 2007). The income from biochemical extraction may considerable. By using this process, latex, serum latex and serum from skim can be utilized perfectly and hence leads to zero discharge scenario from latex industry.

By mixing the skim latex with field latex, it can be treated with papain enzyme and results high quantity of rubber and this was introduced by scientists in Rubber Research Institute, Sri Lanka (Yapa, 1992). The latex is deprotinized by papain and then it can be used to prepare heavy vehicle tires due to less heat emission than conventional tires. Also fungi attack is less than others.

South Korean scientists had researched to recover rubber hydrocarbon to obtain nano composites with organoclay. The approach involved treatment of skim natural rubber latex with alkali and surfactant, leading to creaming of skim latex and removal of clear aques phase before addition of organoclay dispersion. Clay mixed latex was then coagulated to a consolidated mass by formic acid (Alex, Nah, 2006). The resulted rubber had a high gum strength and low amount of organoclay improved the modulus and tensile strength of NR.

2.5 Coagulating agents

2.5.1 Sulphuric acid (H_2SO_4)

Molecular weight of sulphuric acid is 98.07848 g/mol. It is clear, colourless, odorless liquid. Also this is the very strong mineral acid.

This acid is used to coagulate skim latex in rubber industry mainly. Because it is cheaper than all other acids. But there are few drawbacks such as excessive use of sulphuric acid will make rubber tender and easily deteriorate, high acid content will create sulphate problems for treatment systems (Cleaner Technology, 2001).

If high quantity of ammonia is used as preservative of skim, higher amount of acid should be used. Because part of that acid will be used to neutralize the ammonia in latex.

From study of 11 factories, data on sulfuric consumption (kg/ton DRC in skim latex) is as shown in Table.

Table 2.4: Sulfuric Acid Consumption

Factory	Kg/ ton DRC in skim latex
11	120
16	140
10	149
5	208
12	211
1	225
4	227
17	231
2	240
7	326
13	367
Median	211
Min	120
Max	367

Source : (Clear Technology, 2001)

Other than that, this strong acid is used in several industries. Few of them are chemical synthesis, fertilizer manufacturing, oil refining, ore processing. The corrosive properties of sulfuric acid are accentuated by its highly exothermic reaction with water. The

16

danger is obviously greater with more concentrated preparations of sulfuric acid in laboratory. Sulfuric acid is not considered toxic besides its obvious corrosive hazard, and the main occupational risks are skin contact leading to burns and the inhalation of aerosols. Exposure to aerosols at high concentrations leads to immediate and severe irritation of the eyes, respiratory tract and mucous membrane. (http://en.wikipedia.org/wiki/Sulphuric_acid)

Source: (http://www.tannerm.com/lewis.htm)
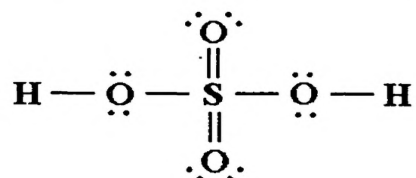
Figure 2.6: Sulphuric molecule

2.5.2 Formic acid (HCOOH)

Formic acid, systematically called methanoic acid, is the simplest carboxylic acid. Its molecular weight is 46.0254 g/mol. It is colourless, fuming liquid. It is used to process organic latex (sap) into raw rubber. The usual commercial product is a solution of 90 percent formic acid in water.

2.5.3 Papain

Papain is an enzyme with iso electric point pH 9.0. The content of this is 15.5% nitrogen and 1.2% sulphur (Singh, 1990). It consists of 212 amino acids stabilized by 3 disulfide bridges. This is a thiol protease which has cysteine residue in the active site (Mathewson, 1998). Papain hydrolyses proteins to form oligopeptides and amino acids. It also contains the proteolytic enzyme chymopapain which differs from papain in electrophoretic mobility, solubility and substrate specificity. The molecular weight of chymopapain is approximately 27000 daltons. Papain has a mild, soothing effect on the stomach and is an excellent aid in protein digestion (http://www.enzymeindia.com/ enzymes/papain.asp).

Papain is usually produced as a crude, dried material by collecting the latex from the fruit of the papaya tree. The optimum pH for the enzyme complex is in the range of 5.0-7.0. The optimum temperature for the enzyme complex is in the range of 55-65 °C.

17

Although papain solutions have good temperature stability, the solution stability is pH dependent. For the active enzyme in solution, the loss in activity is about 1-2% per day, probably as a result of autolysis and/or oxidation (http://www.sigmaaldrich.com).

Source: (http://en.wikipedia.org/wiki/Papain)
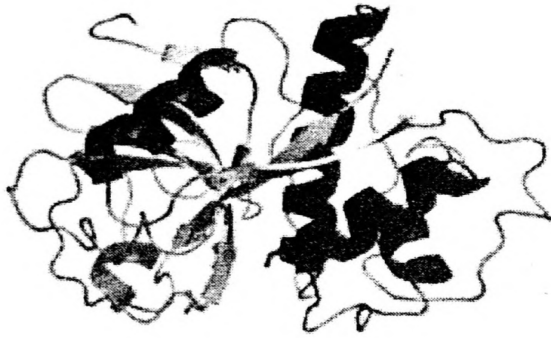
Figure 2.7: Papain from _Carica papaya_

The commercial papain is light brown, grey or weak yellow powder with characteristic taste and smell and posse milk clotting too. A high active product is obtained by dissolving in water, saturating with hydrogen sulphide, precipitating with alcohol and drying the precipitate at low temperature. About 95% of the papain is used in food and beverage industries (Singh, 1990).

2.5.3.1 Deproteinized rubber

Because some _hevea_ proteins have allergenic potential, methods were developed to remove these proteins. An efficient method involves cleaning the latex by centrifugation and employing enzymatic digestion with alkaline proteases or papain or treatment with sodium or potassium hydroxide. This allows production of condoms and latex gloves with low protein contents and the range is less than 20 μg/g of natural rubber (Rose, Steinbuchel, 2005). Crude latex serum is unreliable as a source of allergens, however, because it contains a lot of proteins and other substances other than the allergens themselves. While the variation in allergenic protein levels in different batches of latex has not been investigated, latex proteins in general, and latex enzymes, a class of proteins, in particular, are known to vary with clonal source, season, physiological state of the tree, the intensity of tapping and the use of chemical stimulants to promote latex yield (Cardosa _et al_, 2004).

To manufacture latex-dipped products with reduced soluble proteins, the simplest method is to wash in water. Proteins migrate to the surface of the latex film as it dries and are hence most effectively removed when the film is washed after complete drying.

2.5.4 Aluminium Sulphate (Alum)

Aluminium sulfate is white crystalline solid, widely used industrial chemical. It is frequently used as a flocculating agent in the purification of drinking water and waste water treatment plants, and also in paper manufacturing. In water purification, it causes impurities to coagulate which are removed as the particulate settles to the bottom of the container or more easily filtered. When dissolved in a large amount of neutral or slightly-alkaline water, aluminium sulfate produces a gelatinous precipitate of aluminium hydroxide, $Al(OH)_3$. Aluminium sulfate is sometimes used to reduce the pH. Its can exist with a variable number of water molecules the form being $Al_2(SO_4)_3 \cdot nH_2O$. It dissolves with clear water at the concentration of 1 - 5%. The solution in water is a medium strong acid reacts with alkalis and attacks many metals in presence of water.

2.6 Coagulation

Natural rubber particle is always negative value due to the negative charge of proteins and carboxylic groups surrounding the rubber particle (Sansatadeekul, Sakdapipanich, 2007). Depending on the pH of the medium, H+ or OH- ions may be adsorbed to the hydrated sphere of the protein molecule which covers the rubber particle. Skim is basic due to the presence of ammonia. Then OH- ions attach with water molecules. Then in addition of coagulating agent, water sphere is disappeared and proteins are neutralized in its iso eletric point leading to coagulation.

CHAPTER 3

Materials and Methodology

3.1 Materials for standard tests

3.1.1 Materials for DRC test

3.1.1.1 Chemicals

Acetic acid 2%

3.1.1.2 Equipments

Petri dish

Oven (Memmert, we German)

Filter paper

Funnel

Beaker

Digital balance (Mettler Toledo, China)

3.1.2 Materials for TSC test

3.1.2.1 Equipments

Petri dish

Oven (Memmert, we German)

Digital balance (Mettler Toledo, China)

3.1.3 Materials for COD test

3.1.3.1 Chemicals

Mercuric sulphate

Reagent sulphuric acid (Conc. H_2SO_4 and $AgSO_4$)

Pottasium dichromate solution (0.0417 N)

Ferrous Ammonium Sulphate (FAS)

Ferroin indicator

3.1.3.2 Equipments

Reagent bottles

Pipettes (1, 10, 20 ml)

Burette

Round bottom flask

Watch glass

Water bath

Reflux condenser

3.1.4 Materials for TSS test

3.1.4.1 Equipments

Filter paper (Micro glass fibre - Whatman)

Petri dishes

Digital balance (Mettler Toledo, China)

Wash bottle

Oven (Memmert, we German)

Dessicator

Suction funnel

Measuring cylinder

Spatula

Twiser

3.2 Materials for coagulation

3.2.1 Chemicals

Sulphuric acid (98%, 50%, 10%)

Formic acid (53%, 25%, 10%, 5%)

Papain (10%, 25%)

Aluminium sulphate (0.5 mol/L)

3.2.2 Equipments

Beakers (200ml)

Digital balance (Mettler Toledo, China)

Measuring cylinder (100ml)

Pipette (1, 10, 20 ml)

Dropper

Piece of glass

Funnel

Petri dish

Miller

Spatula

pH meter (MP 220, Mettler Toledo)

Oven (Memmert, we German)

3.3 Methodology for standard tests

3.3.1 DRC Test

Clean Petri dish was weighed (w). About 10g of skim sample(w1) was added and weighed again. Little amount of 2% acetic acid was poured in it and swirled. It was allowed to coagulate for ½ hour and kept in oven at 70 °C for 14 hours. Dried rubber film was allowed to cool, and weighed (w2). Again whole set was oven dried up to 18hours and weighed(w3) as above.

3.3.2 TSC Test

Tare weight of clean empty petri dish was measured(w1). Small amount of skim sample was added in it and weighed(w2). It was oven dried for 2 hours. Latex dish with sample was allowed to cool and dry weight was taken(w3).

3.3.3 COD Test

3.3.3.1 Sample preparation

1ml of skim serum was added to the reagent bottle and diluted up to 100ml with demineralized water.

3.3.3.2 Refluxing

0.4g of mercuric sulphate was added to round bottom flask. Accurate 20ml from prepared sample was poured that. 30ml of reagent sulphuric acid was again added to flask, in water bath. Another 10ml of 0.0417 N $K_2Cr_2O_7$ was mixed with it. Then the round bottom flask was attached with reflux condenser and kept 2 hours under boiling condition. After 2 hours, condenser was washed down by 80ml of demineralized water. The same procedure was followed for blank using demineralized water instead of sample.

3.3.3.3 Titration

To improve the normality of $K_2Cr_2O_7$. it was titrated with standard FAS, which had normality N, in the presence of ferroin indicator till reddish brown end point was reached. The samples and blank in round bottom flasks were titrated with titrant FAS as above using ferroin indicator.

3.3.4 Total Suspended Solids(TSS) Test

Micro glass fibre filter paper was washed with demineralized water without touching. It was laid in a petri dish and kept 2 hours in an oven to complete drying. After 2 hours, petri dish with filter paper was allowed in a dessicator for few minutes to cool. Weigh of both petri dish and filter paper was measured (w1). Then the dried filter paper was carefully taken using a twiser and weighed (w2). Then it was kept in a suction funnel. The measure volume of 25ml of testing serum sample was taken and added to funnel slowly allowing to proceed the filtration under suction. Empty measuring cylinder was washed with demineralized water and added to filter. After completing the filtration, filter paper was carefully taken out using spatula and kept in weighed petri dish. Then the whole set was allowed in an oven for 2 hours. After 2 hours, dish was cooled in a dessicator and the dish and filter paper was weighed (w3) collectively.

3.4 Methodology of coagulation

3.4.1 Coagulation of skim with acids

100ml of skim sample was measured using a measuring cylinder and added to a 200ml beaker. Five samples of skim were prepared like this. Using 98% H_2SO_4, certain amount of acid dosage was weighed and slowly added to a sample. Just after adding, sample was stirred with using a piece of glass for few seconds. Like this way, different quantities of same concentrated H_2SO_4 was added in ascending or descending order of weigh and follow that. Then all samples were allowed for 6 hours. DRC (w1) and TSC tests were done for testing sample.

After 6 hours, coagulated samples were chosen and others were neglected. By decanting the serum, coagulum could be separated. It was milled and washed well. Then the milled product was oven dried for 14 hours. Dried weight was obtained after the drying duration. Then it was further dried up to 18 hours and dried weight (w2) was obtained. Recover yield was calculated.

The maximum recover yield was selected as best. Then allowed time for coagulation was changed fixing concentration and added quantity of acid. Using that, most appropriate settling time was chosen.

COD, pH and TSS were done using decanted serum. By changing the concentration of acids, most suitable dosage was selected. Using above procedure, best conditions of settling time, acid concentration and dosage were chosen. Same procedure was repeated with formic acid and aluminium sulphate.

```
                    Collect skim ◄──────────  Centrifuging plant
                         │              ╲
                         │               ╲──► DRC(w1) and TSC
                         ▼                    tests
                Prepare 100 ml samples
                         │
                         ▼
         Treat with acids ( Formic / Sulphuric, Alum)
                         │
                         │ Change the dosage
                         │ Allow 6 hours
                         ▼
                 Dry and measure yield
                         │
                         ▼
      ┌──────────────────┴──────────────────┐
      ▼                                      ▼
Measure the recover of coagulum      Test COD, TSS, pH of serum
      │
      └──────────────────┐
                         ▼
              Select highest yield (w2)
                         │
                         ▼
Repeat procedure changing coagulating time & fixed dosage & concentration
                         │
                         ▼
    Select suitable coagulating time with highest recovery
                         │
                         ▼
Repeat the procedure to have highest recovery, changing dosage & concentration
                         │
                         ▼
         Choose best conditions for highest recovery
```

3.4.2   Coagulation of skim with papain / acid

Different concentrated papain solutions were prepared and those were mixed with 98% H_2SO_4 with different ratios. Testing sample was tested for DRC (w1) and TSC tests at initially. Testing skim sample was neutralized with 98% H_2SO_4 acid. Using that, 100ml neutralized skim samples were prepared. Then previously prepared papain / H_2SO_4 was used to coagulation. Different quantities of reagent were added to neutralize samples and this quantity may be in ascending or descending order. Immediately adding, samples were stirred with using a piece of glass for few seconds. Then all samples were allowed for 6 hours.

Coagulated samples were chosen and others were neglected after 6 hours. By decanting the serum, coagulum could be separated. It was milled and washed well. Then the milled product was oven dried for 14 hours. Dried weight was obtained after the drying

24

duration. Then it was further dried up to 18 hours and dried weight was obtained. Recover yield was calculated.

The maximum recover yield was selected as best (w2). Then allowed time for coagulation was changed fixing concentration and added quantity of reagent. Using that, most appropriate settling time was chosen which yields higher recovery.

Decanted serum was under gone pH, COD and TSS tests. Same procedure was used by changing the concentrations of reagent and added dosage.

Collect skim ← Centrifuging plant

→ DRC(w1) and TSC tests

↓

Prepare 100 ml neutralized samples

↓

Treat with papain/ H_2SO_4
    Change the dosage
    Allow 6 hours

↓

Dry and measure yield

↓

Measure the recover of coagulum   Test COD, TSS, pH of serum

↓

Select highest yield (w2)

↓

Repeat procedure changing coagulating time & fixed dosage & concentration

↓

Select suitable coagulating time with highest recovery

↓

Repeat the procedure to have highest recovery, changing dosage & concentration

↓

Choose best conditions for highest recovery

3.5 Calculations

3.5.1 Calculations of standard tests

3.5.1.1 DRC Test

Wet weight of rubber $\quad = w1$

Dry weight of rubber film (14 hours) $= w2$

$$DRC\% = \frac{w2}{w1} * 100\%$$

Same calculation was done with 18 hours rubber film. If there was difference between DRC% after 14 & 18 hours, 18hours DRC% was selected for calculation.

3.5.1.2 TSC Test

Tare weight of petri dish $\quad = w1$

Gross weight of the petri dish $\quad = w2$

Dry weight of the petri dish $\quad = w3$

$$TSC\% = \frac{(w3 - w1)}{(w2 - w1)} * 100\%$$

3.5.1.3 COD Test

$$COD = \frac{(V1 - V2) * N * 8000 * 100}{20}$$

V1 = FAS volume for blank

V2 = FAS volume for sample

N = Normality of $K_2Cr_2O_7$

3.5.1.4 TSS Test

Weight of dish and filter paper $= w1$

Weight of filter paper $\quad = w2$

Weight after drying $\quad = w3$

Weight of sludge $\quad = w3 - w1$

TSS $\quad = (w3 - w1) * 10000 \, mg / L$

3.5.2   Calculations of recovery

Dried weight of coagulum $\quad\quad$ = $\quad$ w2

DRC of testing sample $\quad\quad\quad$ = $\quad$ w1

Recover yield of   skim rubber % $\quad$ = $\quad\dfrac{w2}{w1}$ $\quad$ * $\quad$ 100 %

CHAPTER 4
Results and Discussion

Rubber is the main export product in Sri Lanka and its demand and requirements are increased annually. However rubber processing factories generate large amount of waste water containing chemicals, pollutants and various solids. A recent survey indicates that Sri Lanka's rubber processing industry is the nation's largest producer of liquid waste (Tillikeratne, 2007). Skim is the byproduct of field latex centrifuging process, which contains mainly water and 3 – 7% of DRC. It is difficult to coagulate due to high content of ammonia, added as preservative, but can't be discarded. To reduce the troubles arisen after releasing to the environment, skim is coagulated using coagulating agent.

In DPL, CL and skim are collected to separate tanks after centrifuging the field latex. There are eight skim tanks and these are connected together. After completing the filling a tank, it overflows. That overflowing portion is directed to the next tank and this continues process is happened within all tanks. After every 2 hours, centrifuge machines are washed to remove the sludge. The bowl washing is also poured to skim tanks. The washings of floor closer to centrifuge machines are added to that as above. After collecting the field latex from vehicles, bowsers, that containers' washings are put to the skim tanks too. So the testing skim sample is the collection of skim, bowl washing, floor washing. So it is richest with water.

A portion of skim was taken from a skim tank daily. Then the number of samples were prepared from that. Skim collection from tanks was done by randomly. Normally only 3 – 4 tanks are contained skim. Before taking sample, skim in the tank was thoroughly mixed using a specific object, called "Paththa", to obtain homogeneous mixture. Then methodologies were followed.

Table 4.1 : Results with acids

	Quantity for 1000L of skim(kg)	Average yield %	Average TSS (mg/L)	Serum	
				pH	Average COD(mg/L)
98% H_2SO_4	10	98	542	2.6	13744
25% Formic	20	97	460	4.0	15537

Although 98% H_2SO_4 acid yields a 98% recovery, its water quality parameters show pH of 2.6, COD returns of 13744mg/L review poor water quality(Table 4.1). But enzymatic coagulation is more suitable due to its environmental sound result.
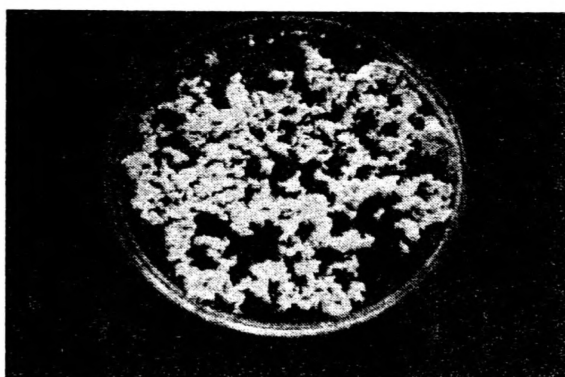
Figure 4.1: Normal coagulation of skim with acid in industry
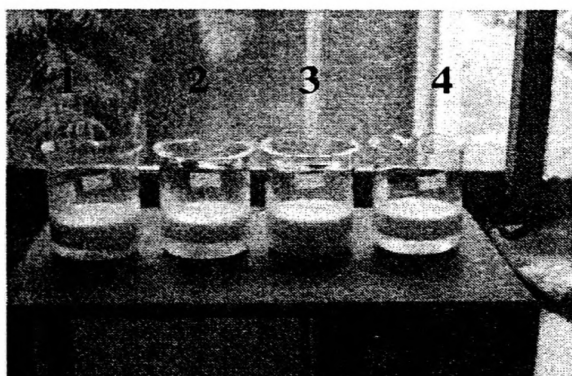
1. 10% Papain / 98% H_2SO_4 coagulation

2. 25% Papain / 98% H_2SO_4 coagulation

3. 98% H_2SO_4 coagulation

4. 25% Formic coagulation

Figure 4.2: Coagulation after 3 hours
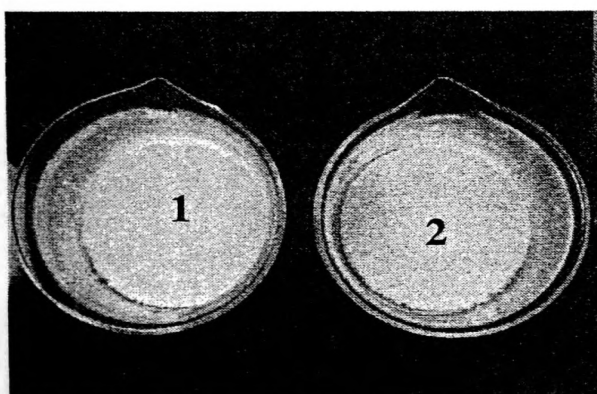
1. 98% H_2SO_4 coagulum

2. 25% formic coagulum

Figure 4.3: Acid treated products

Even though there is large difference between pH of formic and H_2SO_4 acid treated skim serum, COD values are not significantly different(Table 4.1). According to the result, it may cause to higher COD for formic acid treatment. Also H_2SO_4 acid dehydrates the microbes and it initializes the anaerobic digestion in that sample.

Papain, protease, is a protein digesting enzyme of papaya latex which contains number of proteins affect to coagulation process. Scientists of Rubber Research Institute of Sri Lanka had been found a method to produce high quality rubber products with papain. Skim latex is mixed with field latex and reacted with papain enzyme (Yapa, 1992). But this method is not used in commercial level.

Table 4.2 : Results with papain / acid

	Ratio	Quantity for 1000L of skim(kg)	Yield %	TSS (mg/L)	Serum	
					pH	COD (mg/L)
10% Papain:98%H_2SO_4	1:9	2.5	78	386	4.9	11354
25%Papain:98%H_2SO_4	1:19	1.5	79	180	4.8	11553

According to result, 10% Papain/98% H_2SO_4 yields 78% and 25% Papain/98% H_2SO_4 yields 79% of coagulation(Table 4.2).
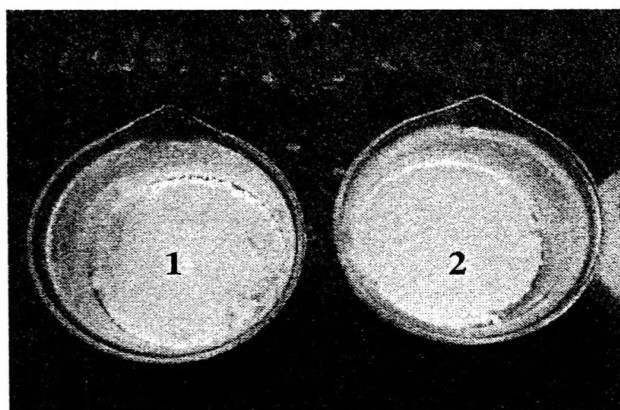
Figure 4.4: Papain treated products

1. 10% papain / 98% H_2SO_4 coagulum

2. 25% papain / 98% H_2SO_4 coagulum

During the coagulation of *Carica papaya* latex, several peptides are processed in an orderly fashion. A lectin like protein called "hevein" the major protein of vacuolar structures in the latex of the rubber tree, is involved in the coagulation of latex by polymerizing rubber monomers (Silva *et al.*, 1997).

In the case of papain and H_2SO_4 acid mixture, it coagulates latex. Both are considered as coagulating agents and in the presence of both, it increases its activity and very small amount is needed. However neutralized medium of skim latex facilitates to enzyme to

exhibit its favorable result. For papain, optimum temperature is 35°C. But temperature controlling was not done, because it was impossible in practical situation in large tanks.

In 1960, Malaysian scientists found that, by removing protein rubber, it can be increased its certain properties. It reduces the heat of heavy vehicles' tires and risk of fungi(Yapa, 1992). In Sri Lanka, papain is recommended for that.

Table 4.3 : Extracted protein levels of products

Sample	EP Level (μg/g)
98% H_2SO_4	710
25% Formic	910
10% Papain:98%H_2SO_4	880
25%Papain:98% H_2SO_4	1010

Extracted protein levels of 98% H_2SO_4 , 25% formic, 10% Papain/98% H_2SO_4 and 25% Papain/98% H_2SO_4 are 710, 910, 880 and 1010 respectively(Table 4.3). But according to obtained result, papain treated products contain higher extracted protein levels than acid treated products. To obtain deproteinised rubber, it should be allowed 48 hours after papain treatment and excess milling than normal procedure.

During the experiment, coagulum resulted by papain was milled without touching to prevent contamination of skin protein. So it may cause to incomplete removal of protein in the result. The higher protein content in skim may cause to such a higher value of EP level in obtained products.

When considering the appearance and texture of the dried products, papain results better coagulum. It was soften mass and light yellowish dried product while H_2SO_4 acid treatment resulted hard mass and dark brown dried product. Formic product was in between of these ends. If excess acid content is added suddenly or accidentally, it may also lead to result deep brown/ black product.

Alum, $Al_2(SO_4)_3$, is a coagulating agent which formed a suspension of rubber, exactly same as the silica suspension in appearance and texture. It was impossible to do any test to that result. During the process of manufacturing gloves, formers are dipped in a coagulant mixture at initial state. If this result of alum can be successively applied in dipping process, coagulant mixture can be rejected. So for further studies, it was directed to R & D laboratory.
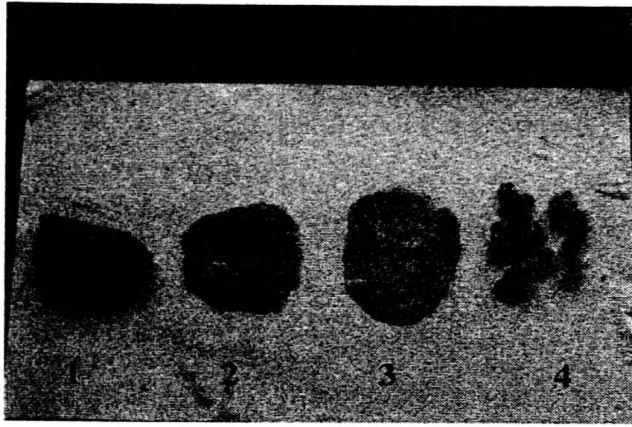
Figure 4.5: Dried products

1. 98% H_2SO_4 product

2. 25% Formic product

3. Papain / 98% H_2SO_4 product

4. $Al_2(SO_4)_3$ product

Natural rubber particle is believed to be covered by some proteins and phospholipids which keeps its stability. So the protein and the dispersion medium is water, the attraction between the water molecules and the numerous hydrophlic groups of the protein molecules results in the latter becoming covered with a water sphere. Although adsorbed ions are removed by adding an electrolyte, alum or acid, still NR particle is hindered by layer of water. In this process, NR particles are stabilized by electrolytic repulsion, can approach closely enough for Vander vaal's force to hold them together (Beagle, 2004). This is caused to well established coagulum and suspension of rubber.

NR Particle

Protein

Water sphere
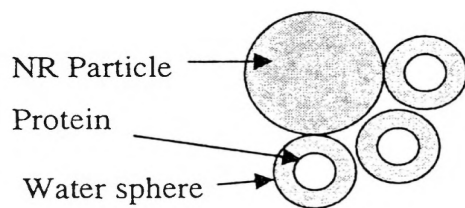
Figure 4.6: Natural rubber particle

Enzymatic coagulation results relatively low yields, but higher cost of papain. Based on the objectives, sulphuric acid coagulation can be chosen as more efficient method to separate skim rubber from skim latex. Due to its perfect settling, easily it can be separated out after releasing the serum from the bottom of the skim tanks. However papain led to interesting phenomenon and further studies can be done.

In DRC test, the resulted value after 14 hours was little bit difference with 18 hours dried weight. Normally in DPL QA laboratory, samples are dried for 14 hours. But QA testing sample and the experimental samples are different in volume and it may not affect to their normal procedure significantly.

Table 4.4 : Difference of DRC values

Sample	DRC after 14 hours	DRC after 18 hours	Difference of DRC%
1	3.762	3.466	7.8682
2	3.923	3.617	7.8002
3	3.616	3.434	5.0332
4	3.606	3.415	5.2967
5	3.907	2.837	27.3867
6	4.314	4.244	1.6226
7	3.719	3.550	4.5442
8	3.194	2.792	12.5861
9	4.410	3.855	12.5850
10	3.716	3.467	6.7008
11	4.000	3.785	5.3750
12	3.868	3.404	11.9959
13	4.006	3.608	9.9351
14	2.896	2.777	4.1091
15	4.382	3.925	10.4290
16	6.066	5.875	3.1487

The difference between these values after 14 and 18 hours is varied as Table 4.4. The composition of field latex may cause to this difference. Because TSC of latex varies from 19% to 45% and it increases with increasing the age of the tree. The protein content decreases with increased age of the tree (Akhtar *et al.*, 1995).

The recovered yield of skim rubber becomes reduce with decreasing the concentration of sulphuric acid and *vice versa*, but not with other coagulating agents. During the acidification, certain amount of acid is used to neutralize the ammonia in the skim sample and remain contributes in coagulation. When added quantity of acid is low, incomplete coagulation may occur resulting poor recovery of rubber.

Table 4.5 : Variation of yield with concentration

	Quantity for 1000L of skim (kg)	Yield %
98% H_2SO_4	10	98
	9	95
50% H_2SO_4	20	93
	15	92
10% H_2SO_4	70	85
	60	83

The analysis of variance was done to determine the highest yield using Minitab statistical analysis package. According to that, 10kg of 98% H_2SO_4 acid for 1000 L of skim yields highest recover as predicted in Table 4.5(Appendix 2). Also the 50% H_2SO_4 acid recovers some what higher level of skim rubber product. Within 95% confidence interval, both means of rubber yield result from 50% H_2SO_4 acid exist and no significant different. But the mean yield from 10% H_2SO_4 acid, differ from others. Also the histogram appears as a bell shape which represents absence of outliers.

In formic acid treatment, the highest recover will be laid in between the range of 98.15% to 96.55% in 95% confidence interval (Appendix 3), when 20g of 25% formic acid is used. But lower concentrations than latter performs relatively low mean yield. The all intervals other than first, overlap confirming that there are no significant difference between yield of skim rubber. The normal plots of both treatments emphasize the approximately normal distribution of residuals.

After completing the coagulation, remain serum can be discharged. This serum can also serve as a fertilizer for rubber and coconut cultivators, because of its relatively high concentration of nutrients like nitrogen, phosphorous and potassium (Yasaratna *et al.*, 2007). Other than that, non rubber components includes proteins, saccharides can be applied as rubber additives and bacterial culture media (Tajima *et al.*, 1995).

Even though this was done within 15 weeks and conclude certain values for maximum coagulation, it can not be said that it is an exact value. Because it may be changed and depends on the centrifugation and other several factors. So in skim industry, optimum acid dosage by daily studies on records and charts and get use of trained officers for scientific adjustments of chemical usage are important (Yasaratna *et al.*, 2007).

Conclusions

98% H_2SO_4 acid recovers highest yield of skim rubber and 25% formic acid results higher recover. When considering both cost and recovered yield of skim rubber, H_2SO_4 acid is better than formic acid.

Papain / 98% H_2SO_4 results low amount of yield, but its water quality parameters are better than others.

With lowering the concentration of H_2SO_4 acid, recover yield of rubber becomes lower and *vice versa*. By considering both yield and required dosage of acid, 98% H_2SO_4 acid is still cost effective than others.

DRC value after 14 hours is further changed, after drying up to 18 hours. It may not affect to standard procedures of DPL QA lab due to their small volume of testing samples.

Recommendations

- If machines are used to mix the skim after adding acids, the effect of mixing time on the coagulation can be detected.

- Acid dosages for skim which results from single, double and triple centrifugations may de different and hence it should be checked.

- Due to the changes of field latex properties, acid dosages detection for skim coagulation is more suitable daily.

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Appendix 1

Selected higher yield of skim rubber from H_2SO_4 acid

Concentration of acid	Quantity for 1000 L of skim (kg)	Yield %
98%	10	99.5
		100.0
		98.7
50%	20	95.3
		93.5
	25	97.2
		93.9
10%	70	82.4
		84.5
		82.0

Selected higher yield of skim rubber from Formic acid

Concentration of acid	Quantity for 1000 L of skim(kg)	Yield %
25%	20	97.8
		97.9
		96.4
	30	88.4
		87.0
10%	100	80.0
		81.3
5%	150	88.1
		81.2
	200	87.5
		89.1

Appendix 2

Analysed result of one way ANOVA

One-way ANOVA: yield 1 versus Sulphuric treatment 1

```
Source              DF      SS      MS       F      P
Sulphuric treatm     3   440.70  146.90   79.01  0.000
Error                6    11.16    1.86
Total                9   451.85

S = 1.364   R-Sq = 97.53%   R-Sq(adj) = 96.30%


                                 Individual 95% CIs For Mean Based on
                                 Pooled StDev
Level  N    Mean   StDev   -----+---------+---------+---------+----
1      3   99.40   0.67                                  (---*--)
2      2   94.39   1.24                          (---*---)
3      2   95.54   2.30                           (---*---)
4      3   82.96   1.31   (--*--)
                          -----+---------+---------+---------+----
                           84.0      90.0      96.0     102.0

Pooled StDev = 1.36
```

```
Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons among Levels of Sulphuric treatment

Individual confidence level = 98.66%


Sulphuric treatment = 1 subtracted from:

Sulphuric
treatment    Lower    Center   Upper
2           -9.324    -5.012   -0.699
3           -8.174    -3.862    0.451
4          -20.291   -16.433  -12.576

Sulphuric
treatment      +---------+---------+---------+---------
2                        (---*---)
3                        (---*---)
4              (---*--)
               +---------+---------+---------+---------
             -20       -10        0        10
```

```
Sulphuric treatment = 2 subtracted from:

Sulphuric
treatment    Lower    Center    Upper    +---------+---------+---------+------
---
3            -3.574    1.150    5.874                            (----*----)         .
4           -15.734  -11.422   -7.109           (----*---)
                                               +---------+---------+---------+------
---
                                              -20       -10        0        10
Sulphuric treatment = 3 subtracted from:

Sulphuric
treatment    Lower    Center    Upper    +---------+---------+---------+------
---
4           -16.884  -12.572   -8.259           (---*----)
                                               +---------+---------+---------+------
---
                                              -20       -10        0        10
```
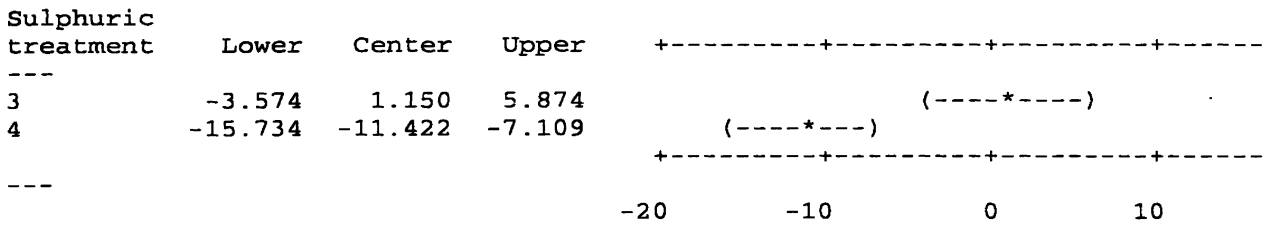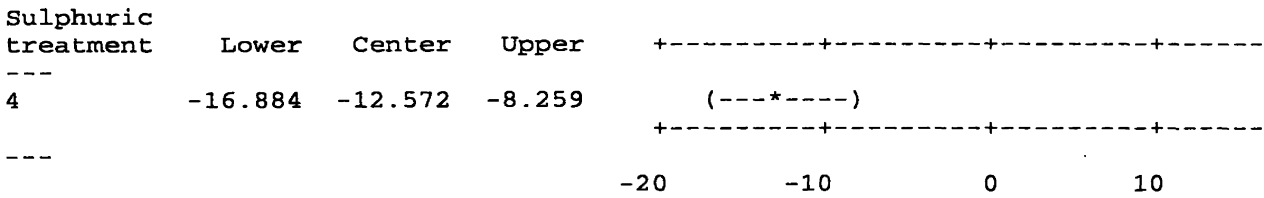
Interpretation of data

$H_0 : \mu1 - \mu2 = 0$; Mean yield is not difference.

$H_1 : \mu1 - \mu2 \neq 0$; At least one mean yield is different from others.

Histogram of Sulphuric treatment
Normal

Mean	2.5
StDev	1.269
N	10

Normal Probability Plot of the Residuals
(response is Yield 1)
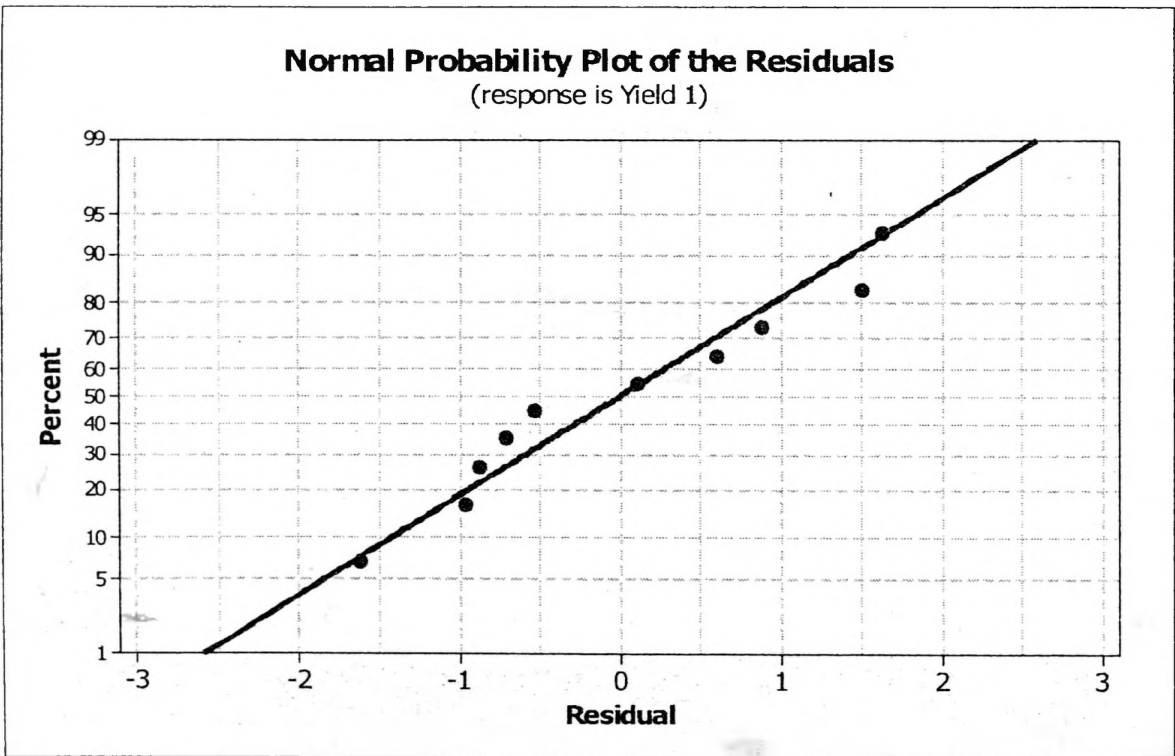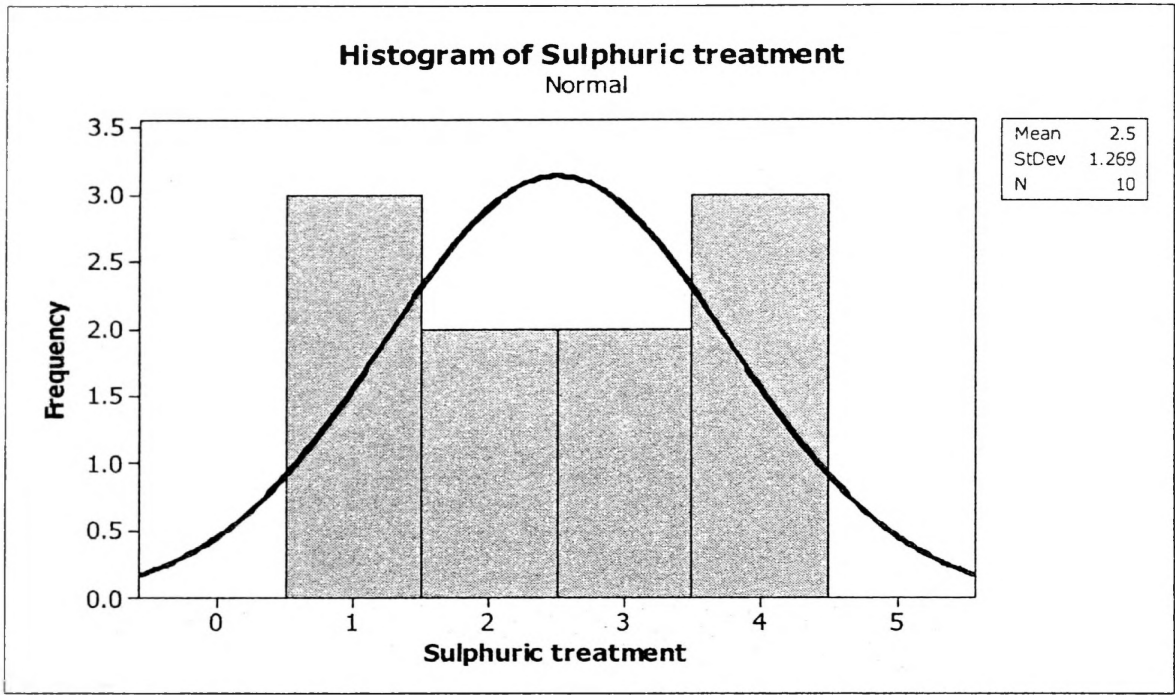
Appendix 3

One-way ANOVA: yield 2 versus Formic treatment

```
Source              DF      SS      MS      F       P
Formic treatment     4   391.26   97.82   20.50   0.001
Error              · 6    28.62    4.77
Total               10   419.89

S = 2.184    R-Sq = 93.18%    R-Sq(adj) = 88.64%


                                Individual 95% CIs For Mean Based on
                                Pooled StDev
Level  N   Mean   StDev    --+---------+---------+---------+-------
1      3   97.35   0.80                                   (----*----)
2      2   87.69   1.00                  (-----*-----)
3      2   80.60   1.01    (-----*------)
4      2   84.64   4.90          (-----*-----)
5      2   88.34   1.14                (-----*------)
                           --+---------+---------+----------+--------
                           78.0      84.0      90.0      96.0

Pooled StDev = 2.18
```
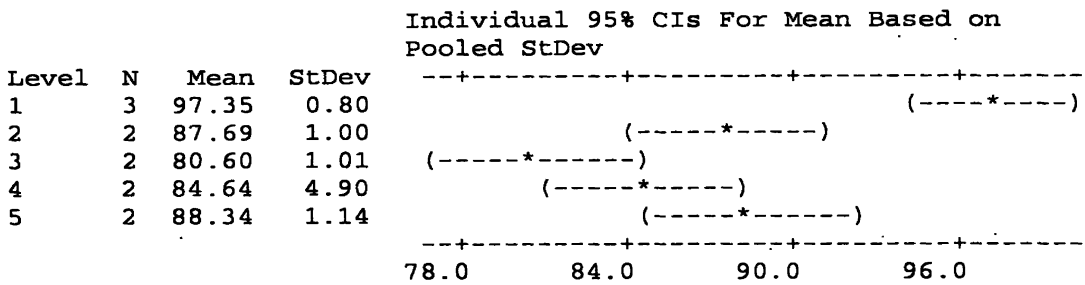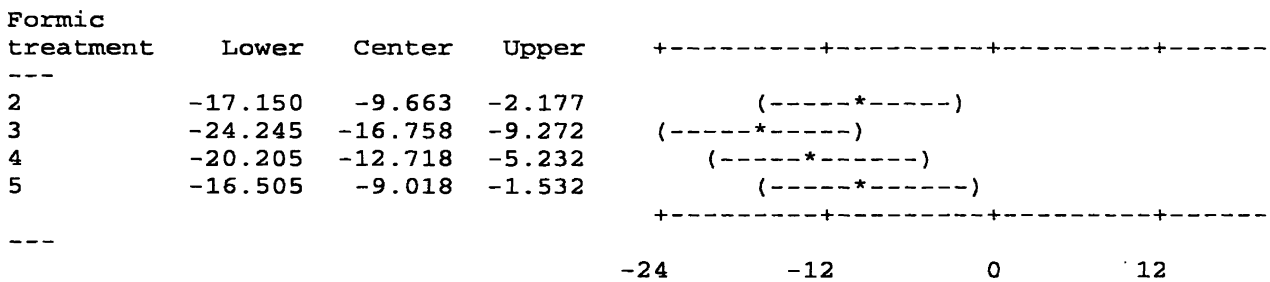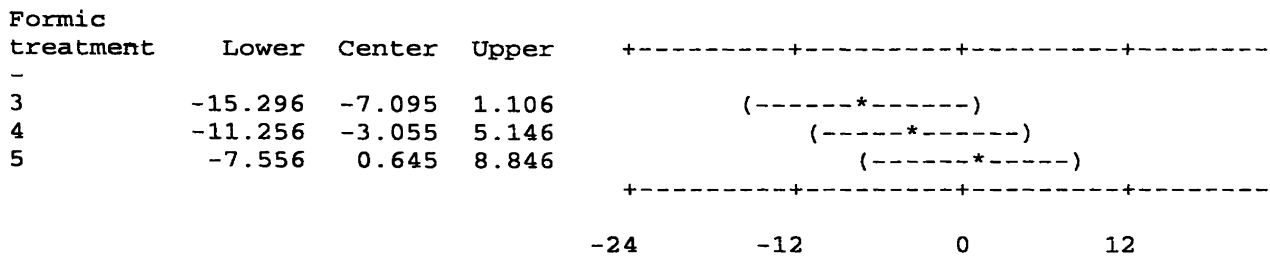
```
Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons among Levels of Formic treatment

Individual confidence level = 99.05%


Formic treatment = 1 subtracted from:

Formic
treatment   Lower    Center   Upper    +---------+---------+---------+------
---
2          -17.150   -9.663   -2.177            (-----*-----)
3          -24.245  -16.758   -9.272   (-----*-----)
4          -20.205  -12.718   -5.232      (-----*------)
5          -16.505   -9.018   -1.532            (-----*------)
                                        +---------+---------+---------+------
---
                                      -24       -12         0        ·12


Formic treatment = 2 subtracted from:

Formic
treatment   Lower    Center   Upper    +---------+---------+---------+--------
-
3          -15.296   -7.095   1.106             (------*------)
4          -11.256   -3.055   5.146                 (-----*------)
5           -7.556    0.645   8.846                     (------*-----)
                                        +---------+---------+---------+--------
                                      -24       -12         0         12
```
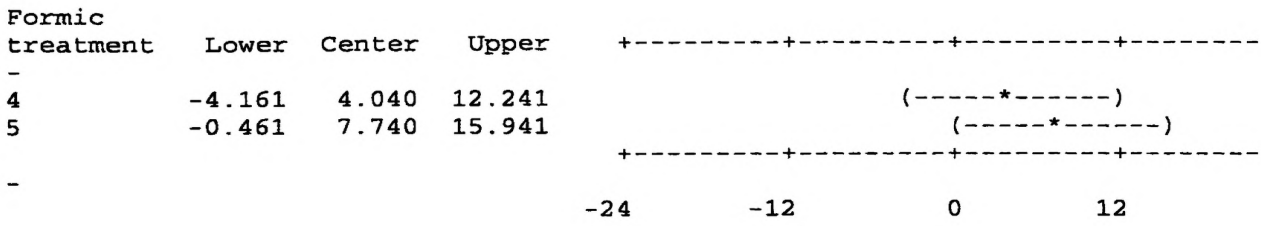
```
Formic treatment = 3 subtracted from:

Formic
treatment    Lower   Center   Upper     +---------+---------+---------+--------
-
4           -4.161   4.040   12.241                         (-----*------)
5           -0.461   7.740   15.941                           (-----*------)
                                          +---------+---------+---------+--------
-
                                        -24       -12        0        12


Formic treatment = 4 subtracted from:

Formic
treatment    Lower   Center   Upper     +---------+---------+---------+--------
-
5           -4.501   3.700   11.901                        (------*------)
                                          +---------+---------+---------+--------
-
                                        -24       -12        0        12
```
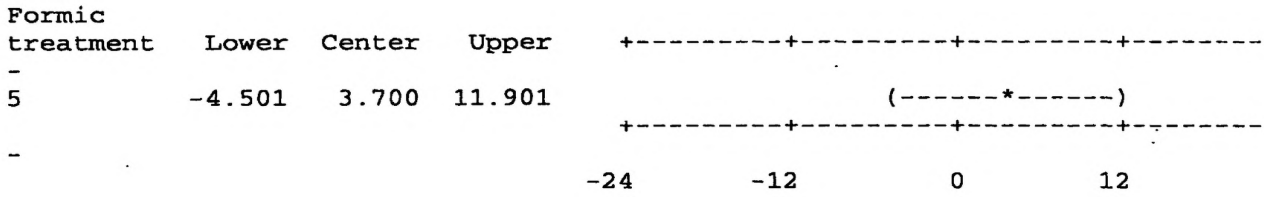
Interpretation of data

$H_0 : \mu 1 - \mu 2 = 0$; Mean yield is not difference.

$H_1 : \mu 1 - \mu 2 \neq 0$; At least one mean yield is different from others.

Histogram of Formic treatment
Normal

Mean 2.818
StDev 1.537
N 11

Normal Probability Plot of the Residuals
(response is Yield 2)

47
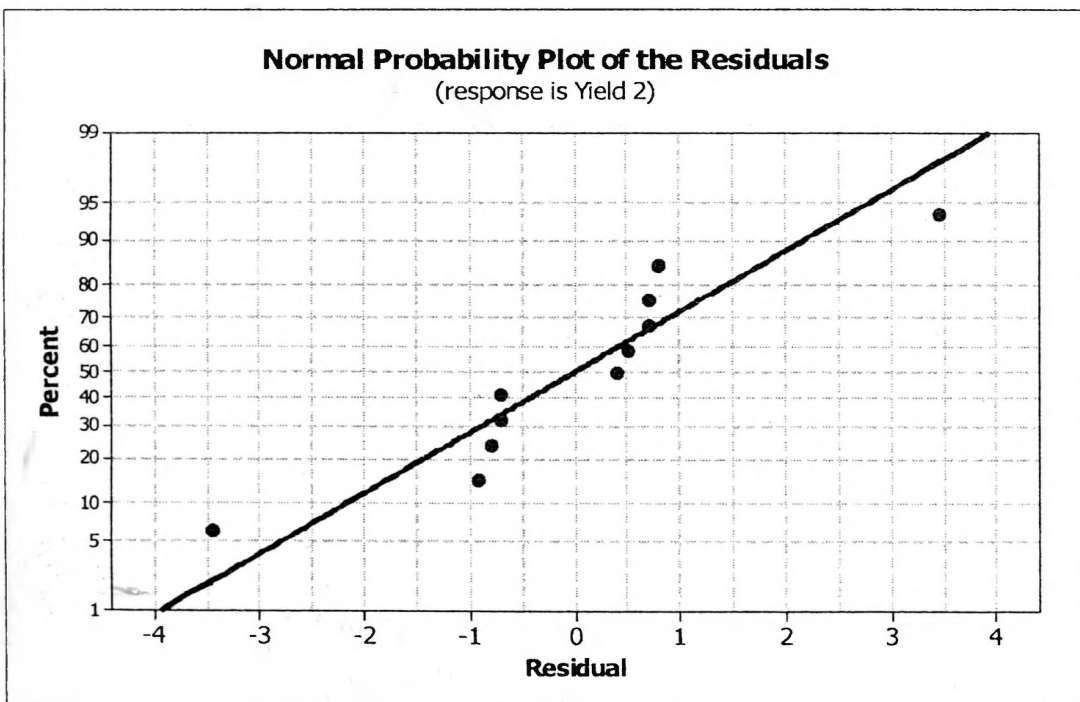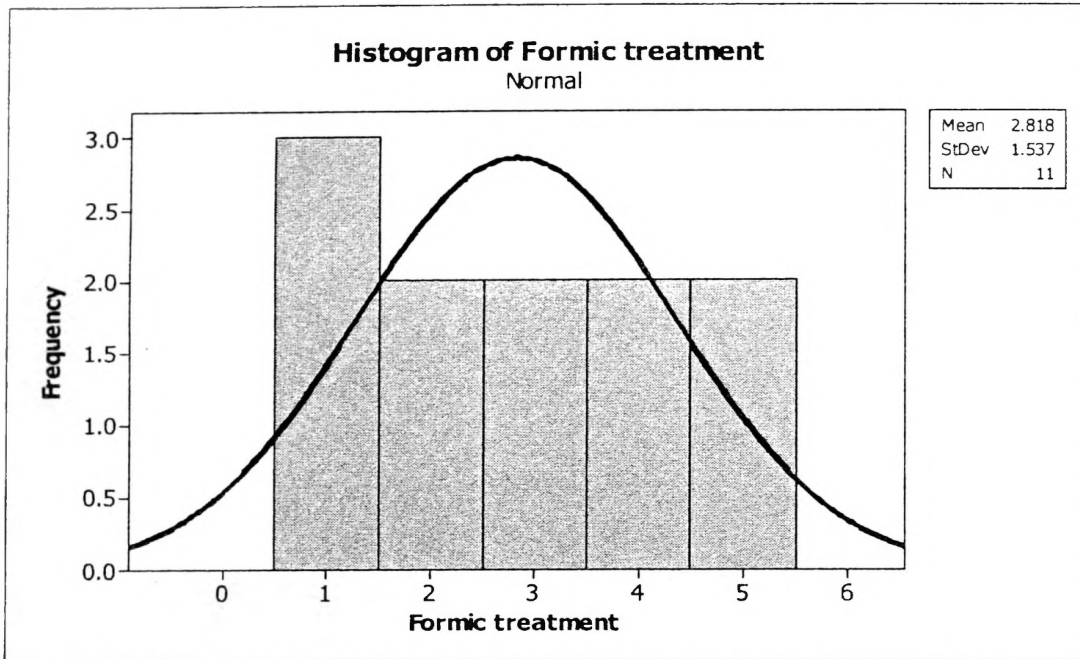
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