# MITIGATING THE IMPACT OF NON-ISOPRENE CONSTITUENTS OF LATEX ON PRODUCT DEGRADATION AND PROCESS EMISSIONS



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BSc. (Hons.)

A Thesis submitted to the Department of Chemical Engineering, Kwame Nkrumah University of Science and Technology, in partial fulfilment of the requirements for the degree of

MASTER OF PHILOSOPHY

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Car

April, 2012.

# CERTIFICATION

I hereby declare that this submission is my work towards the MPhil and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.



(Head of Department) signature date

#### ABSTRACT

This study assessed the impact of chemical and mechanical pre-treatment methods that could be applied in the natural rubber industry with the objective of processodour mitigation and product improvement.

In the chemical treatment, fresh latex were treated with of 1% acids (acetic and phosphoric) sufficient to induce coagulation; 1.0 to 2.0 g/kg.dry rubber of hydroxylamine sulphate salts (HNS); and 0.7 to 4.0 g/kg.dry rubber of copper (II) EDTA chelates separately. The impacts of these chemicals on the utilisation of latex carbohydrates and mercaptans generated during 96 h of natural fermentation have been reported. The effects of these chemicals on the resulting product's Wallace plasticity, Plasticity retention index and Mooney viscosities of each sample were analysed. Hydroxylamine sulphate neither affected the carbohydrates nor the mercaptans generated during the fermentation step. However, acetic acid, phosphoric acid and copper (II) EDTA chelate caused a reduction in the levels of mercaptans and the carbohydrates in the fermenting latex. Hydroxylamine sulphate, acetic and phosphoric acids caused an improvement on the products' Plasticity retention index, whereas all the concentrations of copper (II) EDTA chelate impacted negatively on both Wallace plasticity and Plasticity retention index of products through the oxidation of the polyisoprene itself.

The impact of mechanical pre-treatment was assessed using industrial mills such as slab cutter, macerator and a series of seven creepers in conjunction with a post milling maturation periods of 0, 168, 336, 504, and 672 hours, taking untreated cuplumps (free and agglomerated) as the control samples.

The impact of each of the combinations of mechanical pre-treatment and maturation periods were expressed in terms of Wallace plasticity, Plasticity retention index, Mooney viscosity, colour, degradation kinetics and odour emitted from the process of drying each sample. It was observed that, irrespective of the pre-treatment process or maturation period, heat degradation of processed NR obeys the first order rate law. Mechanical pre-treatment and maturation caused various degrees of improvement in the product properties as well as odour- mitigation depending on the combination of pre-treatment process and maturation period observed. The mechanical pre-treatment by the use of seven crepers became the optimum process since it simultaneously mitigated the odour and improved product properties beyond 336 h of maturation.



## ACKNOWLEDGEMENT

I am very grateful to the Almighty for His grace and guidance towards the successful completion of this work.

Secondly, I wish to express my profound gratitude to Ing. E. Kwaku Baah-Ennumh, my project supervisor, for his guidance and supply of reference materials throughout the period of this research work. I am also indebted to Mr. C. K. Agyente-Badu (NPDU, CRIG), Mr. Edem Bensah Cudjoe (CEESD) and all Lecturers at the Department of Chemical Engineering (KNUST) for their criticisms, suggestions and advice. I also appreciate the comments received from the researchers in UMR IATE (CIRAD) in 2011.

Finally, I am sincerely grateful to my wife for her support towards the completion of this work.



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# LIST OF ABBREVIATIONS

NR	Natural Rubber
ISO	International Organisation for Standardisation
DRC	Dry rubber content
DTNB	5, 5 dithiobis (2-nitrobenzoic acid)
EDTA	Ethylenediaminetetraacetic acid
ISO	International Standard Organisation
μm	micrometer
ppm	parts per million
PRI	Plasticity Retention Index
Po	Initial Wallace Plasticity
Р	Wallace plasticity at any time.
MV	Mooney Viscosity
5L	grade 5, light coloured rubber
5CV	Viscosity stabilised rubber, grade 5.
ln	Natural logarithm.
TGA	Thermogravimetric analysis
IR	Isoprene Rubber
TRIS	Tris (hydroxymethyl)aminomethane

# LIST OF ABBREVIATIONS (continued)

SLO	Sulphur like (Off) Odours
TSR	Technically Specified Rubber
VSCs	Volatile sulphur compounds
HNS	Hydroxylamine neutral sulphate
s.e	Standard error of the mean
s.d	Standard deviation.
	W SANE NO BROME

# **CHAPTER ONE: INTRODUCTION**

The economic importance of the rubber tree (*Hevea brasiliensis*) had long been recognised (Purseglove, 1987) because of its ability to produce latex. The latex has a wide range of applications when processed into latex concentrate (LC), Ribbed smoked sheet (RSS), or the Technically Specified block- Rubber (TSR). The *Hevea* tree is a perennial dicot, made up eleven species. However, *Hevea brasiliensis* is the commercially viable species which does well in the tropical region between 24<sup>o</sup>N and 25<sup>o</sup>S around the equator (Cicero *et al*, 2010). *Hevea brasiliensis* also has a lot of genetic variability (clones) which affords the producer an opportunity to selectively plant specific one in response to the soil (Akpan *et al*, 2007), topology of the planting surface (FELDA, 1989) or desired product characteristics (Yip and Subramaniam, 1984).

There is no doubt that Christopher Columbus and the early Spanish explorers were the first team from Europe to have discovered the use of natural rubber latex for use as balls, containers, and waterproof footwear. Eventhough some samples of the rubber was sent to Spain, the story of rubber was quickly forgotten until rubber was rediscovered by the De la Condamine and Fresneau two centuries later (Loadman, 1995). It is reported that, in 1736, De la Condamine was sent by the Paris Academy of Science on an expedition to determine the exact shape of the earth around Ecuador. Soon after his arrival in Quito, he noted the origin, production and uses of the natural rubber and reported back to the Academy. His report included the words *"Heve"* as the name of the rubber tree, "latex", the milky liquid obtained from the tree, etc.

The present name for the tree which is universally accepted as producing the best rubber is *Hevea Brasiliensis* and this is the source of all modern plantation rubber. It was not, however, the tree which produced much of the rubber spoken of in pre-Columbian times – this was reported to be *Castilloa elastica* which is found north of the Amazon whilst the *Hevea Brasiliensis* is almost completely restricted to an area between the Equator and Lattitude15° South (Loadman, 1995). *Hevea Brasiliensis* was originally called *Hevea Guyahensis* by Fuset-Aublet in 1775, became *Siphonia Elastica* (Persoon, 1807) and finally, *Hevea Brasiliensis* some 60 years later.

It took over hundred years for the development of natural rubber industry after this discovery by the Europeans. Early scientific publication on natural rubber production was attributed to Francois Fresneau, a trained Engineer and additionally a friend of De Ia Condamine in South America. Fifty years after the works of Fresneau, progress was slow until 1820 and 1839, when Hancock (1937) invented his "pickle" machine to convert solid rubber into usable homogenous gum. In the year 1839 Goodyear also discovered "curing" of rubber of rubber using white lead and sulphur that resulted in a highly elastic material. In the United Kingdom, Hancock got hold of some of Goodyear's cured rubber and, identifying sulphur as the "magic" ingredient, developed a curing process which he patented ten weeks before Goodyear (Seymour, 1971; Loadman, 1995). Coincidentally, within the period 1786-1878 five completely separate events in four continents occurred that led to the booming of the natural rubber business. Among them was the invention of four stroke internal combustion engine by Otto in 1876. At the same time, *Hevea* seeds and seedlings "migrated" from America to South-East Asia through Wickham, a British farmer.

Later, some of the seeds were sent to Africa; Aburi gardens- Ghana (1893), Camayenne garden-Guinea (1897), and the garden of Ebute-Meta, Nigeria (1898).

Since then, natural rubber has been an indispensable commodity in the civilisation of the world through the use of automobiles, machine parts, etc. Several attempts have been made to substitute natural rubber with synthetic rubber because natural rubber cultivation is restricted to the tropics but consumed principally in temperate regions. These attempts led to the production of synthetic isoprene rubber that are supposed to be similar to natural rubber, because isoprene is the building blocks of natural rubber. However, to date, all synthetic rubber produced by this means is reported to be insufficient in some desired product-properties when compared to natural rubber (Tuampoemsab, 2008; Mark *et al*, 1998).

Several properties of natural rubber make it very useful as a commodity for the fabrication of a number of items for both industrial and domestic purposes. Among them are the high tensile strength, high tear strength and good elasticity. These important mechanical properties make rubber the single most useful commodity in the fabrication of train-coaches, construction of bridges, roads, subways, doors and hinges, tyres, footwear and several components of the automobile industry. This usefulness of natural rubber makes it a very significant foreign exchange commodity for some of the Asian and African countries like Malaysia, Thailand, Vietnam, India, Cote d'Ivoire, etc.

In Ghana, the rubber industry has become a source of income to most residents living in over fifty (50) communities in the Western, Central and the Eastern Regions. For the past forty years, the communities have benefited directly through the operations of GREL and RPG, the two major producers of natural rubber in Ghana. The communities have benefited through their main operations, contributions to community-based projects and also through their Outgrower projects- where farmers are assisted to cultivate their own plantations.

However, there are several challenges in the rubber industry. Among them are the storage hardening of processed natural rubber (Eng *et al*, 1994; Nimpaiboon, 2008), microbial growth upon storage (Linos, 2000), susceptibility to oxidation by heat and non-isoprene constituents of latex (Tuampoemsab, 2008), and the emission of odour along the stages of NR processing (Danteravanich *et al*, 2007(a)). Despite the economic importance of the rubber industry, communities around the rubber processing factories usually object to the odour generated by the rubber processing operations. Though, the odour has not yet been proven to be a health hazard, its nuisance is enough to justify the concerns raised by the immediate communities and towns within which NR processing goes on. In particular, in the study area, opinion leaders and inhabitants in the nearby communities have expressed some concerns about the nauseating smell emitted from the processing facility (GNA, 2010). If the odour emission concerns are not addressed in time, it may adversely affect the relationship between the rubber factories and their surrounding communities.

Several points on the line of production have been identified as the origin of the characteristic odour associated with NR (Danteravanich *et al*, 2007(b)). Taysum (1958) and Lowe (1960) were part of the early researchers who characterised the causative agents of the coagulation step and attributed it to bacterial infection, growth, and metabolism. They concluded that the interaction between the bacteria and the latex components produce the acidic media which finally coagulates the lattices into cuplumps, leaving an odorous serum as a by-product.

Recent studies confirm the presence of odorous constituents of both the field coagulated-cuplump and the latex grades (Wongniramaikul *et al*, 2008). The focus of

this research work is to simultaneously improve product characteristics and mitigate odour associated with the natural rubber production through either chemical or mechanical pre-treatment along the stages of production.

### **1.1 OBJECTIVES**

Odour and product degradation continue to be the most serious challenges in natural rubber industry the world over. This study therefore seeks to study and propose the effective ways of mitigating the effects of non-rubber constituents of latex responsible for odour emission and product degradation. Hence this research work seeks to:

- I. Assess the effect of chemical pre-treatment of latex on latex carbohydrates, mercaptans generation and product characteristics.
- II. Assess the impact of mechanical pre-treatment on the final product characteristics and process-odour emission at the study area.

The specific objectives of this research are:

- I. With respect to assessing the effect of chemical pre-treatment of latex on carbohydrates, mercaptans generation and product characteristics, the following specific objectives are to be achieved:
  - a) to ascertain the effect of acid addition on the latex-carbohydrates and mercaptans generation during latex fermentation.
  - b) to assess the effect of copper (II) EDTA chelates on mercaptans levels and carbohydrates during the latex- fermentation step.
  - c) to assess the effect of hydroxylamine sulphate salt (HNS) on the latex carbohydrates and the level of mercaptans generated during fermentation.

- II. With respect to mechanical pre-treatment on the final product characteristics and process-odour emissions,
  - a) the impact of mechanical pre-treatment on physical properties of natural rubber (Wallace plasticity, PRI, Mooney viscosity, colour, degradation kinetics) would be assessed.
  - b) the appropriate unit operation (and hence the equipment) for the mechanical pretreatment of cuplumps would be evaluated.
  - c) an environmentally friendly process modification in rubber processing with inherent reduction in phosphoric acid consumption would be specified.
  - d) the optimum maturation period that gives the best product characteristics and less odour emission would be specified.

## **1.2 SCOPE OF WORK**

Although odour emissions and product quality associated with NR production has received the attention of Scientist and Engineers recently, all the authors and contributors so far have focussed their works on either the origin of the development of the odorous compounds (Fulton, 1993), or the analytical methods for characterisation of the compounds (Wongniramaikul *et al*, 2008; Danteravanich, 2007(a)). In contrast to the earlier works, this work is an attempt to investigate and hence propose a method for simultaneous improvement of product characteristics and process-odour mitigation.

In order to ascertain unit operations on the process line, where the odour mitigation and product improvement plan could be effected, the scope of work encapsulates chemical pre-treatment and its impact as one part and mechanical pretreatment and its impact on the other part. Thus, chemical pre-treatments would be tried at the pre-coagulation stage of the latex whilst mechanical pre-treatments would be performed at the post coagulation stage of the field coagulated latex (cuplumps).

# **1.2.1** Part I. The impact of chemical pre-treatment of latex on latexcarbohydrates, mercaptans and product characteristics.

The presence of non-isoprene constituents such as carbohydrates, proteins and amino acids make natural rubber latex susceptible to natural fermentation. Like all fermentation reactions, the constituents and conditions of the substrate play an important part in the fermentation process. Therefore, the latex pH were adjusted by the use of varying amounts of acetic acid, phosphoric acid, and hydroxylamine neutral sulphate whereas different amounts of copper (II) EDTA were also introduced to sequester any mercaptans present and produced in the course of the fermentation.

Whilst acetic acid, phosphoric acids and hydroxylamine sulphate are common chemicals used in rubber industry for the coagulation of latex, improvement in PRI and the production of constant viscosity rubber respectively, copper (II) EDTA chelates were introduced in the method for experimental purposes.

Subsequently, the impacts of these chemicals on the process of fermentation were followed through the determination of carbohydrates. Likewise, the extent to which mercaptans were generated during the process of fermentation was monitored and used as a target constituent responsible for malodour generation. Moreover, the quality of the natural rubber after the treatment was assessed and subsequently used as a measure of the suitability of the chemical for the odour mitigation.

# **1.2.2** Part II: The impact of mechanical pre-treatment on the final product characteristics and process-odour emissions.

After natural coagulation of latex in the plantation, natural rubber obtained from the solid coagulum (cuplumps) was subjected to different mechanical pretreatment processes and maturation regimes. This was to assess the effect of the several combinations of pre-treatment and maturation periods on the product characteristics and odour emission levels.



# **CHAPTER TWO: LITERATURE REVIEW**

### 2.0 NATURAL RUBBER GRADES AND USES

Natural rubber (NR) is mainly used by tyre manufacturing industries. Other uses are for manufacture and fabrication of footwear, transmission belts, conveyors, clinical gloves, train coaches, etc. There are several regional and national standards for grading processed NR, but the most accepted standard at the international level is ISO2000. Under this standard, NR is graded based on the source or nature of the original raw material at the factory, together with other physical and chemical properties (technical specifications) like Wallace plasticity, Plasticity retention index, Mooney viscosity, etc. That is, in a natural rubber processing factory, the process line for the production of field grades (TSR10, TSR 20 and TSR50) require a naturally (field) coagulated cuplumps, which serves as the raw material whereas the required feed-stocks for the process line for the latex grades (TSR5, TSR-5CV) must be liquid- latex. Thus, natural rubber could be produced by naturally field coagulated cuplumps, when the field grades are required, or by acid-aided coagulation in the factories by the use of acids when the latex grades are required.

# 2.1 COMPOSITION AND PROPERTIES OF NATURAL RUBBER LATEX.

Natural rubber is made up of isoprene units and has an outstanding mechanical properties compared to the synthetic rubber as shown in Appendix 1. Natural rubber is obtained from coagulated latex. *Hevea* latex is a colloidal suspension of polyisoprene and other particles dispersed in an aqueous solution.

Early researchers reported that the tree sap of *Hevea* has three types of particles dispersed in the liquid phase. They are the rubber hydrocarbon, the Frey-Wyssling particles (Frey-Wyssling, 1929), and the globular particles named lutoids

or viscoids. In 1953, Cook and Sekhar were the first to have attempted to separate the latex-particles into fractions by means of ultracentrifugation. Their work was continued later by Moir (1959) under controlled conditions which resulted in the identification of several distinct fractions after centrifugation. Recent studies have confirmed that at least ultracentrifugation can separate the colloidal solution of latex into four main parts based on visual judgment (Tuampoemsab, 2008). They are the Rubber fraction, the Frey-Wyssling particle, the serum, and the bottom fraction. The components are as given in **Tab. 2.1** below.

Table 2.1 The composition of *Hevea* latex

FRACTION	COMPONENTS
Rubber Fraction	Proteins, Lipids, Metals
Frey Wyssling particles	Lipids, Carotenoids
Serum fraction	Proteins, Amino acids, carbohydrates
Bottom fraction	Proteins, Metals, Others

Source: Tuampoemsab, 2008.

Earlier works indicated that, the variation in the exact quantity of each component are driven by factors such as type of clone, the age of the tree, exploitation method, rainfall seasons, soil factors, and even planting material (Chin *et al*, 1979; Subramaniam *et al*, 1980; Habibah *et al*, 1986; Dibi *et al*, 2010).

# 2.1.1 The rubber fraction

The rubber fraction is made up of the hydrocarbons, which is reported as being mainly cis-1, 4 polyisoprene (Moir, 1959). Tuampoemsab (2008) confirmed that each rubber particle was covered by a double adsorbed layer of protein and phospholipids, which plays an important role in the stabilisation of the rubber particle in the serum phase by carrying a negative charge. Earlier reporters also indicated that rubber particles are also associated with traces of triglycerides, sterols, sterol esters, tocotrienols, and other lipids (Hasma and Subramaniam, 1986).

# 2.1.2 Frey-Wyssling particle

These are non-isoprene particles found in between the rubber fraction and the serum fraction after centrifugation of latex, named in honour of Frey-Wyssling who was the first to identify them in 1929. It has been reported that the Frey-Wyssling particles contain mainly lipids and carotenoids.

#### 2.1.3 The serum fraction

The serum fraction contains the water soluble substances such as proteins, amino acids, carbohydrates, and some inorganic ions. The presence of amino acids in NR latex was first reported in 1925, subsequently several studies in this area are far advanced. Yong and Singh (1975) investigated into the mean content of the prominent amino acids present in the latex as shown on **Tab. 2.2** below.

Another very important non-isoprene constituent is carbohydrates, which is an essential substrate in natural fermentation. The sugars in the serum are reported to be mainly L-quebrachitol or 2-o-methyl-L-inositol, with minor quantities of glucose, galactose, and fructose (Tuampoemsab, 2008). Some of these carbohydrates are decomposed by bacteria into the fatty acids, by the time they are separated from the serum (Akiyama *et al*, 1991).

Amino acid	Mean content	
	% of latex serum.	
Analine	0.004	
Glutamic acid	0.033	
Glycine	0.009	
Valine	0.006	ICT
Lysine	0.005	151
Tryptophan	0.004	
Leucine	0.003	12
Serine	0.003	
Aspartic acid	0.002	
Histidine	0.001	A HI
Arginine	0.001	
Total of amino acids	0.107	

# **Table 2.2** Amino acids present in NR latex

Source: Yong et al, 1975.

# 2.1.4 The bottom fraction

Lutoids forms the bulk of the bottom fraction. They are spherical membrane bound bodies and are mostly larger in size than the rubber particles. Lutoids is very rich in phosphatidic acid (Southorn *et al*, 1968). Trace metal is one of the mineral components found in NR latex. It has been reported that latex contains sodium, potassium, calcium, magnesium, rubidium, manganese, copper, silicon, sulphur, and phosphorus (Belmas, 1952). **Tab. 2.3** on the next page shows the average percentages of metal content found in NR latex. It is also remarkable that trace elements such as copper, manganese and iron play an important role of pro-oxidant or oxidative catalyst in the degradation of rubber, however their effect on the selective oxidation of thiols group of compounds responsible for odour generation, has not been established.

Table 2.3 Percentages of metal in natural rubber latex.

Metal symbol	Ca	Mg	K	Na	Fe	Cu	Rb	Mn
Mean value	0.002	0.001	0.2	0.007	0.006	0.0002	0.002	trace

Source: Belmas, 1952.

# 2.2 EXPLOITATION OF THE HEVEA TREE

The production of natural rubber starts from the exploitation of *Hevea* trees in the plantations. The exploitation process is done by a systematic cutting of the tree bark through the cambium in order to open up the latex vessels. This action causes the latex to flow out of the trees which are collected in latex-cups. The cycle is repeated every 3-5 days based on the tapping system adopted by the plantation. After tapping, the liquid-latex may be collected from the cups and transported to mills for the production of the latex grades; or they may be allowed to coagulate- naturally (in the cups) for about three to four days in order to produce field/cuplumps grade rubber. When latex is allowed to coagulate in the cups at the plantations, the solid coagulums obtained is also called cuplumps. Thus, the cuplumps becomes the feedstock for the processing of the field grades whereas the liquid-latex is a feedstock for the processing of the latex grades.

#### 2.3 NATURAL RUBBER PROCESSING

As indicated earlier, natural rubber processing leads to either the latex grades (TSR 5L, TSR 5CV) or the field grades (TSR10, TSR20 and TSR50). The typical process flows for the production of both grades are as shown at Appendix 2(a) and Appendix 2(b) for the latex and cuplumps process lines respectively.

## 2.3.1 Coagulation of latex

Coagulation is the process of destabilisation of the latex in which few lumps of the polymer rigidly separate from the latex and remains as a semi-solid, suspended in the medium which is known as serum. The coagulum itself contains a network of isoprene polymer with a variable amount of entrapped serum (Harris, 1980). Coagulation is therefore done to recover the rubber from the latex and impart other technical properties onto the final product (Lau, 1980).

As said earlier, there are two ways of coagulating latex depending on the intended grade (latex or field) to be produced. For the latex grades, the coagulating agents are usually weak-organic acids, mineral acids or sometimes a mixture of organic acids and other product-characteristics enhancing agents such as hydroxylamine sulphate salts (HNS). Acids applied are used to coagulate the latex rapidly in order to by-pass the natural fermentation stage. Not only does the acid increase the rate of coagulation, but additionally changes the medium pH which finally affects the microbial population and hence the fermentation reaction itself (De Mora *et al*, 1986; Monk, 1986). However, it is a common knowledge that latex will coagulate when its pH is lowered sufficiently below 5.2. That is, acid addition could cause latex to coagulate directly without the completion of natural fermentation.

Several coagulation equipment are employed these days for the production of the latex grades, The complexity and the technology used depend on the size of the raw material. Small scale coagulation may use coagulation tanks made from aluminium, concrete or stainless-steel. Large scale industrial holdings normally employ bulking tanks together with coagulation troughs which makes use of matchflow system.

However, for the production of the field grades, natural or spontaneous coagulation of the lattices are employed. This is achieved when the lattices are allowed to coagulate naturally in the collection-cups, right in the plantations, under the action of microbes. Collection cups employed vary between 0.3-1liter capacity depending on the age and the yield of the trees. Natural coagulation has been attributed to the effect of fermentation of the non-rubber constituents present in the latex, thereby producing acidic media which finally effect coagulation (Akiyama *et al*, 1991).

## 2.3.2 Fermentation of latex prior to coagulation.

The presence of carbohydrates, amino acids, nitrogen and nutrients like phosphorus makes it an ideal substrate for spontaneous fermentation under natural conditions. Firstly, like all fermentation reactions, constituents such as carbohydrates, proteins, amino acids, and trace elements have a huge direct influence on the characteristics of the coagulum obtained after fermentation through these components becoming a substrate for the microbes.

Secondly, in a complex matrix of nutrients and microbes, such fermentations reactions are usually associated with several side reactions (Zoecklein, 2007). Among the key products of the side reactions are mercaptans (Van *et al*, 2007) and

several other fatty acids and nitrogen containing substances (Wongniramaikul *et al*, 2008; Danteravanich *et al*, 2007).These non-isoprene units in the coagulum could impact on the physical properties (Po, PRI, Mooney viscosity, colour), the degradability by heat and microbes, and finally the kind of odour emitted during production.

Microbial population in latex is so diverse and it ranges from bacteria (both facultative and obligate), fungi, etc. Taysum (1960) identified some key microorganisms present in the latex and traced their origin into the lattices. He reported that the bacteria seemed intimately associated with the latex vessels on the panels of trees even before tapping of the latex. He therefore concluded that bacteria infections were from two main sources. That is, the external portions of the tree-bark and the latex vessels. He found also that there were several types of bacteria including *Serratia marcescens* (an obligate aerobe) and *Bacillus megaterium* (a strongly aerobic strain incapable of growth under strictly anaerobic conditions). Other bacteria found were microaerophilic forms that are strong acid-producing including *Streptococcus, Lactobaccillus, Clostridium* species, and *Streptococcus* species.

The relationship between latex composition and the final coagulum matrix is very complex. Yeast and most bacteria depend on sugars, amino acids, vitamins, inorganic ions, lipids for its metabolism and ends up producing a whole host of other substances that were not part of the original latex (Wongniramail *et al*, 2008). That is, the main difference between the field grades and the latex grades starts from the constituents of a fermentation media which express themselves through their impact on the yeast or bacterial and hence fermentation rate (Bamforth *et al*, 2003).

Natural fermentation leads to the production of organic acids and alcohols which may be odorous or pre-cursors of the odour active compounds. The spectrum of odour active materials produced by yeast or bacteria depends on the medium in which it is growing, both via the medium impact on the extent of microbial growth and on the metabolic fluxes within microbes (Bamforth *et al*, 2003).

A lot of work has been done on the origin of malodours associated with NR processing environment. Danteravanich *et al* (2007) confirmed the presence of several fatty acids and esters in naturally coagulated rubber which were not part of the original latex. They also reported of the presence of organic acids like acetic, propionic acid, isobutyric, butyric, isovaleric and valeric which are part of the causative agents of the unpleasant odours associated with rubber factories. Tuomola *et al*, (2000) also reported that apart from the fatty acids originating from the carbohydrate material, other sulphur and nitrogen containing proteins and amino acids present in the serum could also be the cause of the odour when proteins are degraded by microbial fermentation.

# 2.3.2.1 Formation of alcohols and esters during fermentation

In addition to ethanol, yeast produces long chain complex alcohols (Dickinson, 1998; Bamforth, 2003). These are important aroma compounds in all yeast fermented compounds and have interesting organoleptic properties in their own right. It is a common knowledge that yeast converts sugars to alcohol using the glycolytic pathway. In addition, it produces a number of long-chain and complex alcohols such as isoamyl alcohol, 'active' amyl alcohol, isobutanol, 2-phenyl ethanol and tryptothol.





Source: Sakdapipanich et al, 2006.

Thus, carbohydrates in latex can also be microbiologically oxidised to volatile fatty acids (VFA) partly responsible for odour generation (Galli *et al*, 2002).

Gee and Ramirez (1994) also derived a relatively straight forward equation to explain the production of volatiles during fermentation such as higher alcohols and esters as below:

In the formation of esters,

$$\frac{d(IA_C)}{dt} = Y_{IAC} \mu_{IA} X$$
 Equation(1)

Where:

IA= concentration of isoamyl acetate

 $Y_{IAc}$  = yield coefficient

 $\mu_{IA}$  = specific rate of isoamyl alcohol formation

*X*= yeast concentration.

From this equation, it is evident that the rate of production of ester such as isoamylacetate is inherently dependent on the production of its precursor, isoamyl alcohol and on the yeast concentration. All of which adds on to the pool of volatile matter in the fermentation media. Thus, the extent of odour compounds produced depends largely on the microbial population and activity.

Secondly, Gee and Rimerez (1994) observed that, there is the possibility of the formation of higher alcohols as suggested in the equation below:

$$\frac{\partial(IA)}{\partial t} = Y_{IA/S} \mu_X X \frac{K}{K+L} + Y_{IA/E} \mu_L X \qquad \text{Equation (2)}$$

Where: *IA*= the concentration of isoamyl alcohol  $Y_{IA/S}$ = the yield of isoamyl acohol by synthetic pathway  $Y_{IA/E}$ = the yield of isoamyl alcohol by Ehrlich pathway  $\mu_X$ = the specific yeast growth rate. *X*= the yeast concentration

*K*= inhibition constant for leucine

*L*= leucine concentration

 $\mu_L$ =the specific rate of leucine uptake

Therefore, the production of isoamyl alcohols is affected by the rate of yeast growth (which depends on various factors) and by the presence of inhibitors that block the biosynthetic pathway. It is apparent from these equations that, relevant factors are the amount of yeast present, its conditions and ability to grow (specific growth rate).

More importantly, this equation illustrates that the amount of ester is a direct consequence of the extent to which the precursor higher alcohol is produced. Moreover, the equation illustrates the importance of the levels of individual amino acids such as leucine (Dikinson *et al*, 2000).

Esters prominent in coagulated natural rubber media includes the several C6-C10 medium chain fatty acids methyl esters (Isa *et al*, 1991; Danteravanich *et al*, 2007(b)). It is noteworthy that, the technological parameters affecting the production of esters can be divided into three categories: those related to micro-organisms characteristics (strain, physiological state), those related to fermentation conditions such as pH, etc. and more importantly, the fermentation method. Esters are also important not only that they are compounds that produce their own smell, but also act as a precursor for the production of other odorous compounds.

# 2.3.2.2 Production of sulphur-like off odours (SLO) in fermentation media.

Other fermentation related compounds that are of immense interest are the forms sulphur sometimes takes under anaerobic conditions. These reduced sulphur compounds, sometimes called volatile sulphur compounds (VSCs), are usually foul-smelling in very minute quantities in all sugar fermenting systems if not controlled (Monk, 1986; Van *et al*, 2007). Natural fermentation microorganisms are the cause of the formation of hydrogen sulphide ( $H_2S$ ) and mercaptans. The mechanisms involved in the formation of the hydrogen sulphide ( $H_2S$ ) and mercaptans depend much on the fermentation temperature and the medium pH value (Wenzel and Dittrich, 1983; Monk, 1986; De Mora *et al.*, 1986).

Sulphate is brought to the cell and reduced to sulphide via two ATP activation steps. At this point sulphide is combined enzymatically with nitrogen containing carbon precursors to ultimately form cysteine and methionine, two sulphur containing amino acids. This sulphate reduction sequence is activated to produce sulphide whenever there is a metabolic demand for cysteine and methionine. That is, all organic sulphur compounds are formed via sulphur containing amino acids. In the absence of intercellular nitrogen, this reduction sequence can continue leading to the formation of excess  $H_2S$  which is not incorporated into amino acids, but liberated into the fermenting medium. Therefore a high rate of sustained  $H_2S$  production can be observed in response to nitrogen deficiency (Zoecklein, 2007).

Subsequently, large quantities of the  $H_2S$  generated in young sugar fermentation media after fermentation may lead to nauseous sulphur-linked smells from hydrogen sulphide and mercaptans (Schutz and Kunkee, 1979; Wenzel *et al.*, 1980; Maujean *et al.*, 1993; Rauhut and Kurbel, 1994). It has been well documented in literature that  $H_2S$  will form mercaptans if left untreated after fermentation. However, copper (II) treatment could be effective against hydrogen sulphide and mercaptans (Zoecklein, 2007; Robert *et al*, 2010).

Another very important group of sulphur-like-odours are the sulphides, disulphides and thioesters. Sulphides and disulphides can be formed from the oxidation of mercaptans. Disulfides can smell bad (sometimes worse than mercaptans) but they usually have higher detection thresholds than mercaptans. Thioesters, however, are odourless but can undergo hydrolysis to release more mercaptans, thus contributing to disagreeable odours. Since the sensory thresholds of mercaptans are relatively low, and therefore smell at very low concentrations (ETS laboratories, 2011; Powers, 2004), mercaptans were therefore selected as the target compounds for monitoring odours generated from the chemical pre-treatment experiments in this work.

#### 2.3.2.3 Mitigation of sulphur-like odours in fermentation media

It is well documented in literature that copper (II) ions could be used to treat  $H_2S$  and some mercaptans whereas disulphides and thioesters do not react with copper (II). As indicated by Robert *et al* (1994), Cu (II) reacts with mercaptans to form Cu (II)-thiol complexes, Cu (II) is reduced to Cu (I), and the thiols are oxidized to the corresponding radicals. Two of the radicals can react to form a disulphide and Cu (I) reacts with a second thiol to form a Cu (I)-thiol complex.

With the affinity of copper (II) for mercaptans or thiols known (Keller *et al*, 2002; Zoecklein *et al*, 1999), then the mercaptans found originally in latex can be oxidised by copper (II). This makes copper (II) very important for this work especially when no correlation exist between copper (II) and ageing properties of natural rubber.

# 2.4 MATURATION AND BLENDING

After natural coagulation of latex in the plantations, the coagulum obtained (cuplumps), are allowed to mature before processing. Storage of the raw cuplumps from the time it is supplied from the plantation to the day of processing is termed maturation period. Maturation periods in most factories range from seven days to thirty days depending on the supply and the availability of raw materials. After the maturation period, different cuplumps received from different locations and suppliers

are blended or mixed together to reduce the variability that may exist among the different deliveries.

It is reported that *Hevea* latex undergoes several biochemical changes after it emergence from the tree through processing, storage, till they are finally consumed in the secondary manufacturing industries. These changes have been attributed the interaction between the polyisoprene chain and some "abnormal" groups that exist on rubber molecule such as epoxide (Burfield, 1974), aldehyde (Subramaniam, 1976, 1977), esters (Eng *et al.*, 1994) and other non-rubber constituents such as free-amino acids and proteins (Subramaniam , 1984) that were initially part of the latex matrix. These biochemical chain reactions finally affects the molecular weight of the polymer and hence the Wallace plasticity and Mooney viscosities.

## 2.5 SIZE REDUCTION

Several combinations of machines are installed in response to the type of raw material being handled. These machines generally reduce the size from 6cubic centimetre to about 0.3 cubic centimetres necessary for optimum drying.

#### 2.6 DRYING

All processed natural rubber are dried in either a continuous or quasi-batch dryer whose operating conditions are normaly set at 120 °C  $\pm$ 10 °C for a total cycle time of 3-4 hours depending on the type of raw material (latex or cuplumps), the capacity or the type of the dryer. Dried rubber can now be tested for the rubber properties, pressed into standard unit of bales 35 kg or 33.3 kg, based on customer's specifications. Most of the natural rubber odours have been attributed to the drying stage of processing (Danteravanich, 2007(a)).
#### 2.6.1 Psychophysical methods of evaluating odour emitted during drying

For several years now, psychophysical methods have been used to establish the functional relationship between the physical and the physic (mental) worlds. Thus, psychophysical methods establish the relationships that exist between the physical stimulus coming from the environment and the human sensations. Unlike vision and audition, where the physical stimuli have been clearly defined, olfaction is still a subject whose stimulus is still not clearly known (Koster, 1984). First the "threshold" is not an absolute value, but a statistical concept. Thus, there is no physical intensity that constitutes the breaking point under which no stimulus could be detected or above which all stimuli are perceived (Koster, 1984; 1985). In this regard, instead of absolute threshold, detection threshold is rather used. Accordingly, the detection threshold is defined as the concentration at which a subject detects an odour with a probability of 0.5 (Powers, 2004).

Secondly, since the detection is based on the subject's ability to detect, the detection threshold is affected by ones conditions and circumstances such as - adaptation to the stimulus, response bias, illnesses, satiation (hunger/satisfied), fatigue, hormonal influences, age, etc (Koster, 1984). It is therefore important that methods used in evaluating industrial odours take care of the inherent challenges associated with olfaction. In most research on odour pollution, samples of the emitted gas are taken at the same source and the concentration expressed in terms of the dilution factor necessary to reach the detection threshold. Once the concentration is known, dispersion models are applied to estimate the emission concentrations from the source, and in different directions taking into account the prevailing climatic conditions and the geographical profile (Clarenburg, 1987; Ubeda, 2010). Although

the dispersion model approach is quite useful, these models do not represent the extent of nuisance experienced by the population (Koster, 1985) - which is of interest in this work. Thus, knowledge of odour strength does not provide a direct indication of the degree of annoyance provoked by the odour. However, methods that have been proven to be effective in the evaluating of industrial odours on a large scale are those developed and tested with the help of population panels (Koster *et al*, 1985; Maiwald *et al*, 1989; Perrin *et al*, 1989; Punter and Blaaubroek, 1989).

Population panels are group of volunteers who have committed themselves to give judgements on nuisance of odour. Population panels work with precisely constructed scales (Koster *et al*, 1985; Punter *et al*, 1984) to indicate the degree of annoyance experienced. Panels members are carefully selected to form a group that is representative as possible of the total population with respect to sex, age, socio-professional background, time spent in the area, dependence on industry and attitude with regards to environmental problems, etc.

#### 2.7 HEAT AGEING / DEGRADATION OF PROCESSED NR.

The impact of heat on processed rubber is very important to all the NR producing factories. For this reason, any odour mitigation method should not have an adverse effect on the heat ageing properties of the resulting product.

It is a common knowledge that processed NR undergoes considerable changes during and after processing. Thus, external temperatures could cause condensation of aldehydic groups (cross-linking) or oxidation (chain scission) of the polypropylene backbone depending on the temperature conditions. Thus, whereas temperature below 60°C causes cross-linking in natural rubber, higher temperatures tend to initiate chain scission in the isoprene polymer (Ballau *et al*, 1981; Keller *et* 

*a*l, 1982; Abu-Zeid *et al*, 1986; Sambhi, 1989).These changes finally affect the degradation rate and hence the Plasticity retention index which is the very important parameter for NR processors. Thermal properties are significant because most of the downstream processing techniques (e.g. tyre manufacturing) are carried out at elevated temperatures. The physical properties and technological performance of the rubber produced are thus influenced by their thermal resistance (Cunneen *et al*, 1978; Le Roux *et al*, 2000).

There are several methods of assessing the impact of heat on natural rubber. Ozawa (1965), Flynn and Wall (1966) expressed the thermal resistance and kinetics at elevated temperatures using the thermo-gravimetric (TGA) measurements in order to ascertain the thermal behaviour of the natural rubber. Though thermo-gravimetric analysis technique can be used to quickly obtain the activation energy and additionally characterize the polymer in terms of the dependence of the decomposition temperature on heating rate , it has been reported that the degradation observed through TGA involves quite different processes (such as, volatilization of small molecule fragments, formation of amorphous carbon, etc.) than the oxidation of the unsaturated backbone of the polyisoprene responsible for the loss of failure properties of interest herein (Ozawa, 1965; Flynn, 1978; Le Roux *et al*, 2000; Mott and Roland, 2001). Sambhi (1989) however, explained that the intrinsic viscosity,  $\eta$ , of NR solutions at  $30 \pm 0.01$ °C is directly related to the Wallace plasticity through the equation (3) below:

$$\eta = bP + c \qquad Equation (3)$$

Where P = Wallace plasticity; b and c are the slope and the intercept of the  $\eta$  versus P plots respectively.

It is well established in literature that molecular degradation is the main process occurring during the high temperature oxidative ageing of most commercial grades of natural rubber (Sambhi, 1982). Additionally, the degradation, measured in terms of Wallace plasticities, exhibits first-order kinetics. Thus, first-order rate constant of degradation could be used to characterize the heat degradation pathway of natural rubber polymer (through chain- scission) to their corresponding low molecular weight compounds (Barnard, 1963; Sambhi, 1989). The degradation rate could therefore be expressed as below:

$$\frac{dP}{dt} = k(P)^n$$

Where, n=1 for first order kinetics.

Rearranging we obtain:

$$\frac{dP}{P} = -kdt$$

Integrating both sides from ageing time, 0 to t, we obtain:

$$\ln(P) = -kt + \ln(P_0)$$

Where: *t* is the time of ageing,

*P* is the plasticity at any time, *t*,

*Po* is the initial Wallace plasticity (Ageing time, *t*=0), and

*k* is the rate constant of degradation.

Therefore a plot of ln(P) versus t for various samples of NR could generate the rate degradation constant, k as slopes of the straight line which could be used to assess the

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Equation (6)

Equation (5)

Equation (4)

thermal degradation or chain scissions of natural rubber at the test temperature of 140°C.



# **CHAPTER THREE: METHODOLOGY**

#### **3.0 MATERIALS AND METHODS**

This study was designed to focus on pre-treatment of the raw material either by chemical or mechanical means with the main objective of product improvement and process-odour mitigation. The experiments were therefore to exploit a means of simultaneously improving the product properties and mitigate odour emissions. All experiments were repeated six times, spread around the year. The periods of the experiments were grouped into three seasons. Namely; September- October, January-February, and June - July in order to have representative samples that reflect the transition, dry and rainy seasons in Ghana.

## **3.1 MATERIALS**

### 3.1.1 Chemicals

The chemicals used in this study are listed in the Tab. 3.1-Tab. 3.3 below.

Table 3.1	. Process	chemicals
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CHEMICALS	SUPPLIER	GRADE
Copper sulphate	BDH	GPR, 98.5%, min
Acetic acid	VWR	Anala <b>R</b> ,99.8% min
Phosphoric Acid	BDH	GPR 95% min
Hydroxylamine sulphate	Chemique	85%,min

# Table 3.2 Chemicals used in phosphoric acid test

Chemicals	Supplier	Grade
1. Tris(hydroxymethyl)aminomethane	Sigma-Aldrich	99.8%
2. Ammonium Molybdate	Sigma-Aldrich	83%,ACS
tetrahydrate		
3. Ammonium metavanadate	Sigma-Aldrich	99%, ACS
4. EDTA	Sigma-Aldrich	99.4% min
5. Trichloroacetic acid	Sigma-Aldrich	99.0%, ACS

 Table 3.3 Chemicals used in carbohydrates tests.

Chemicals	Supplier	Grade
Tege X	1888	
1. Nitric acid	BDH	AR, 65%
2. Sulphuric acid	BDH	95%, min
3. Sucrose	Sigma	99.5, min
4. Anthrone	Sigma-Aldrich	97%, ACS
5. EDTA	Sigma-Aldrich	99.4% min
6. TCA	Sigma-Aldrich	99.0%, ACS

 Table 3.4 Chemicals used in mercaptans tests.

Chemicals	Supplier	Grade
1. Glutathione reduced	MERCK	98%
2. 5,5 Dithiobis (2-nitrobenzoic acid)	Sigma	98%, ACS
3. EDTA	Sigma-Aldrich	99.4% min
4. TCA	Sigma-Aldrich	99.0%, ACS
	ICT	

## 3.1.2 Instruments

All measuring equipment and tools were calibrated based on manufacturer's instructions. The uncertainty of all measuring instruments was also taken into consideration.

 Table 3.5 Instruments used in Spectrophotometric analysis

Instrument	Supplier	Model
1. Spectrophotometer	Thermo electronic	Genesys 20 (±0.001)
2. pH meter	Hanna	8424 (±0.01)
3. Vortex mixer	Stuart	SA8 (5-1500rpm)
4. Magnetic stirrer	Stuart	Stir/ CB 161 (10-1000rpm)
5. Water bath	Memmert	M210 (max, 95°C)
6. Analytical balance	Mettler	AE100 (±0.0001g)
7. Centrifuge	Hermle	Z160M (14000rpm, max)

Fable 3.6	Other	testing	instruments
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Ins	strument	Uses	Supplier	Model
1.	Plastimeter	Wallace plasticity	Wallace Inst.	MKV(±0.01)
2.	Ageing	PRI	Wallace Inst.	O14(140°C ±0.5°C)
	chamber			
3.	Viscometer	Mooney viscosity	Alpha tech.	MV2000 (±0.1)
4.	Air circulating	- KVII	Advantage Lab	AL-01-05-100 (max,
	oven		551	250°C)
			A	

#### **3.2 EXPERIMENTAL METHODS**

#### **3.2.1 Experimental design for chemical pre-treatments**

In order to understand the impact of the fermentation step on the production of mercaptans, about 98 kg of freshly tapped latex was collected in a cool-box and temperature maintained around 4°C using ice cubes. The latex was then sent to the laboratory immediately. The bulk latex was subdivided into 250 g each and stored in a latex-cup. One set of the latex in the cups was subjected to natural fermentation leading to natural coagulation. This was the control samples from which the amount of total carbohydrates and mercaptans were monitored every 24 h for a period of 96 h.

For the other parts of the latex, several quantities of chemicals were added to the latex and their impacts were monitored. Chemicals tried in this experiment were copper (II) EDTA chelate, hydroxylamine sulphate, phosphoric acid and acetic acid. A schematic representation of the experiment is as shown in Fig. 3.1 below.



Figure 3.1 Scheme of experiment for chemical treatment.

The details of methods used in the treatment of latex with the chemicals are as follows:

#### 3.2.1.1 Treatment of latex with hydroxylamine sulphate.

Three different cups were taken and labelled. 250 g of latex were then transferred into each cup. Each 250 g sample of latex was treated with already prepared 1% solution of hydroxylamine to form a treated-latex mixture whose concentrations of HNS in the latex mixture were: 1.0 g/kg.dry rubber, 1.5 g/kg.dry rubber, and 2.0 g/kg.dry rubber. These treatments were selected to cover the concentrations applied by most producers of constant viscosity rubber. Detailed calculations are as presented in Appendix 3. Each of the treated latex was then

homogenised by stirring for about 2 minutes. After homogenisation, each of the treated latex was then allowed to coagulate under ambient conditions  $(29\pm3)$  °C for 96 hours. During the 96 hours of the experiment, the samples were prevented from rainfall and direct sun rays. Sampling was done on the fermenting media every 24 hours and tested for latex carbohydrates and mercaptans.

#### 3.2.1.2 Treatment of latex with acid coagulants.

250 g sample of latex was weighed and transferred into a 500 ml conical flask. The latex contained in the flask was placed on a magnetic stirrer. During stirring, a calibrated pH meter was introduced into the latex. Whiles stirring and the pH meter in position, already prepared 1% solution of acetic acid were introduced into the latex from a burette. The acid was added until the pH of the latex-acid mixture was equal to 5.2, which is an industry norm for the coagulation of latex. This corresponded to an acid concentration of 5.3 g/kg.dry rubber. Another two 250 g latex samples were treated in order that the concentrations of acetic acid in the latex-acid mixture were 6.7 g/kg.dry rubber and 13.3 g/kg.dry rubber. The samples were then allowed to coagulate for 96 hours at ambient conditions (29±3) °C. During the 96 hours, samples were drawn every 24 hours and analysed for total carbohydrates and mercaptans.

The same process above was repeated using 1% solution of phosphoric acid also. Thus, a 250 g of latex were treated with 1% phosphoric acid solution until the latex-phosphoric acid mixture attained a pH equals 5.2. When the mixture attained this pH, the concentration of phosphoric acid in the latex mixture was 13.3 g/kg.dry rubber. However, acid concentrations of 5.3 g/kg.dry rubber and 6.7 g/kg.dry rubber were prepared in order to be able to perform a comparative analysis between the two acid coagulants. Detailed calculations are as described in Appendix 4.

#### 3.2.1.3 Treatment of latex with copper (II) EDTA Chelate.

250 g of latex was treated with copper (II) EDTA chelate to make a mixture whose copper (II)EDTA concentration were 0.7, 1.3, 2.0, 2.7, 3.3 and 4.0 g/kg.dry rubber (Sample calculations are as provided in Appendix 5). Each latex sample was then homogenised by stirring and allowed to coagulate under ambient conditions (29±3) °C for 96 hours. During the 96 hours of storage, samples were drawn from the fermentation media every 24 hours and analysed for total carbohydrates and mercaptans.

# 3.2.2 Extraction of non-rubber components from fermentation media for carbohydrates and mercaptans tests.

1 litre of an extracting solution made up of 5 % trichoroacetic acid and 0.2 % EDTA was prepared, labelled and stored in the refrigerator. About 5 ml of the sample is taken and centrifuged at 4000 rpm to separate the serum from the other particles in latex. 1 ml portion of the serum obtained from each of the samples from the chemical treated latex were each added to 10 ml of the extracting solution. Each extracting solution together with its corresponding sample was allowed to stand for ten (10) minutes before they were filtered across a filter paper. The filtrate became the extract from which total carbohydrates and mercaptans were determined by spectrophotometry.

#### **3.2.3** Experimental design for mechanical pre-treatments

A ten (10) tons sample of 3 days field coagulated cuplumps from GT1 clone of *Hevea brasiliensis* plantation located near Agona-Nkwanta in the western region of Ghana were collected and divided into five (5) lots (approximately 2 tons each). With the exception of the control samples (Agglomerated and free-cuplumps), each lot was taken through the mechanical pre-treatment process shown in the Fig. 3.2 below.

The output of each of the processes was stored independently at ambient temperatures and normal atmospheric pressures. Each lot was also protected from direct sun rays. Lots were stored for a total of twenty eight days within which samples were drawn from the bulk samples for processing and testing as follows: processing immediately after sample collection in the field (0 h); seven days later (168 h); fourteen days later (336 h); twenty-one days later (504 h) and twenty-eight days later (672 h). With the drying conditions set at 120°C for 2 h.30 min. Samples were tested for product characteristics such as Wallace plasticity, Plasticity retention index, Mooney viscosity, colour, heat degradation rate, and odour emitted during drying. Figure 3.2 Scheme of experiment for mechanical pre-treatment.



3.2.3.1 Control samples for mechanical pre-treatment

**Free cuplumps:** This lot was achieved by the use of wheel-loader to spread fresh cuplumps so that the bulk of the cuplumps are subjected to aerobic conditions.

**Agglomerated lumps:** This lot was generated by heaping the freshly received cuplumps at a specific location so that they agglomerate. That is, subjecting this sample to anaerobic conditions during the maturation period from 0 h through 672 h (Ehabe *et al*, 2002).

#### **3.2.4** Processing of mechanically pre-treated samples after maturation

After maturation, each sample was subjected to the normal processing of natural rubber cuplumps as shown in **Fig. 3.3**.

About 2 kg of each rubber sample was milled and crept into a thickness of 6 mm - 8 mm. Each crepe was shredded into fine crumbs. Each shredded sample was then divided into three portions for treatment with 0%, 1% or 2% phosphoric acid solutions. 0.5 kg of each portion was then immersed in a 20 liter solution of a specific phosphoric acid concentration for a total of 5 minutes. After 5 minutes, the sample is left to drain for a total of 2 minutes before drying. All crumbs were dried in an oven pre-conditioned at  $120 \,^{\circ}C \pm 5 \,^{\circ}C$  for 2 h.30 min as pertaining in the industrial dryer.

Pre-treated NR Maturation (0 h, 168 h, 336 h, 504 h, 672 h) Milling Phosphoric acid treatment NR Characterisation Drying Odour Assessment

Figure 3.3. Processing and analysis of mechanically pre-treated natural rubber.

**3.2.5** Processing equipment used for mechanical pre-treatments

Machines used were one Slab-cutter (Jumbo type), a macerator (Coarse creper) and a serially arranged seven crepers (details are provided in Appendix 3).

#### **3.3 TEST METHODS**

#### **3.3.1** Determination of total carbohydrates in latex during fermentation.

Dreywood's method of the determination of sugars with anthrone in a strong sulphuric acid was used in the determination of trace amount of carbohydrates during latex fermentation. Sucrose was used as a model compound for the colorimetric determination of sugars in NR using spectrophotometer. The absorbance readings were carried out at 627 nm to get a relationship between standard concentrations of sucrose and absorbance readings at 627 nm in the presence of anthrone reagent. The absorbance was plotted against the carbohydrate concentrations to get a calibration curve. Extracted samples containing the non-rubber components were also acidified and treated with anthrone reagent and their absorbance readings recorded. The samples concentrations were then deduced from the calibration curve knowing their specific absorbances.

#### 3.3.2 Determination of mercaptans in latex fermentation media.

5-5'-dithio bis(2-nitrobenzoic acid) also known as DTNB or Ellman's reagent was used to react with the free sulphydryl side chain of mercaptans to form a S-S bond between the mercaptan and a thionitrobenzoic acid residue. The reaction was performed at pH 7.0 - 8.0 by the addition of dilute trichoroacetic acid solution. Standard solutions of glutathione (GSH) were used as a model compound and their absorbance at 412 nm were recorded when reacted with Ellman's reagent. A calibration curve of GSH concentration and absorbance reading were obtained as shown on Fig. 4.2. The non-rubber components extracted from the samples were subjected to the same treatment with Ellman's reagent at same pH of 7.0 - 8.0. Their absorbance readings were then recorded accordingly. The samples concentrations were then deduced from the calibration curve knowing their absorbance.

#### **3.3.3** Determination of %phosphoric acid by molybdate method.

Analytical grade phosphoric acid was used as a standard for the colorimetric determination of phosphorus by the Molybdate method (Dibi *et al*, 2010). The results obtained from the standard solutions of phosphoric against that of the corresponding absorbance readings at 410 nm were used to generate a calibration curve. The curve was used to deduce the concentration of all unknown phosphoric acid solutions using its model equation.

#### **3.3.4** Determination of Plasticity and Plasticity Retention Index

The Po and PRI of the raw NR samples were determined by Wallace Plastimeter according to ISO 2007 and ISO 2930. A constant compressive force of 100 N  $\pm$  1 N was applied on a rubber pellet prepared for 15  $\pm$  0.2 seconds. The thickness of the specimen at the end of this period was measured automatically by a pre-calibrated Plastimeter. One Wallace Rapid Plasticity unit represents a change in thickness of 0.01 mm. As required by ISO 2007 and ISO 2930, each sample was tested thrice and the median value computed as the Wallace plasticity. The PRI value was determined by the percentage ratio of the initial Wallace Plasticity, *Po* and *P*<sub>30</sub>. The *P*<sub>30</sub> was obtained after oxidative ageing of the three test pieces, with a Wallace ageing chamber pre-conditioned at 140 °C  $\pm$ 0.2 °C for 30 minutes.

The equation for the determination of Plasticity retention index (PRI) is as shown below:

$$PRI = \frac{P_{30}}{P_0} \times 100$$
 Equation (7)

#### 3.3.5 Determination of heat degradation rate of processed NR

Each of the pre-treatment samples (Agglomerated, Free cuplumps, Slab-cut, Macerated, and Crept blankets) were subjected to Wallace plasticity analysis after accelerated ageing in a Wallace ageing chamber pre-conditioned at 140 °C for 0, 5, 10, 15, 20, 25, 30 minutes. A plot of logarithm of plasticities obtained as against a specific time gave the isothermal heat degradation model similar to those reported by Sambhi (1989) whose slope is the degradation rate constant in the Arrhenius equation. Heat ageing kinetics provides an idea as to the technological performance of processed natural rubber at elevated temperatures.

#### 3.3.6 Determination of colour index of processed NR.

The colour index of a sample was determined based on ISO 4660. A Comparator System based on visual comparator with a lighting unit to guarantee correct lighting conditions for colour grading through matching was used. The samples were prepared from a homogenised test piece whose final thickness was within 3.2 mm - 3.6 mm. Each pellet was wrapped in polyester film and placed in a mould. The samples in the moulds were pressed in a press whose lower platen and upper platen temperature were set at 150 °C  $\pm$  3 °C and a working pressure of 3.5 MPa. The resulting sample was stripped off the polyester film, and then placed in the comparator instrument for colour matching. Samples were then matched against graded (numbered) coloured glass filters in the Lovibond test discs. The colour on the filter that matches that of the test pellets was recorded as the colour of the sample.

#### 3.3.7 Determination of Mooney viscosity of processed NR

Mooney viscosity was determined by the resistance (expressed as torque) offered by a rubber sample to a rotor turning at 2 r/min  $\pm$  0.02 r/min, when the lower platen and upper platen forming the cylindrical chamber is maintained at 100 °C  $\pm$  0.5 °C during the test period. The resistance offered by the rubber to the rotation is expressed in arbitrary units as the Mooney viscosity (ML, 1+4) when the viscometer is calibrated to read zero Mooney units when the machine is run empty and 100  $\pm$  0.5 when a torque of 8.3 N.m  $\pm$  0.02 N.m is applied to the rotor shaft by the rubber sample. That is 1 Mooney unit is equivalent to 0.083 N.m of torque exerted on the rotor shaft.

Two pieces of homogenised samples were placed at the upper and the lower of the Viscometer rotor. The upper platens were lowered when their temperatures were at 100 °C to begin the pre-heating period. After one minute of pre-heating the sample between the platens, the motor was started for the test to run for four minutes. At the end of the four minutes, the Mooney viscosity is displayed as a digital value on the machine.

#### **3.3.8** Determination of *pH* and temperature of latex.

The pH and temperature of the collected latex were determined using a calibrated pH-meter (Hanna8424) by direct reading. A calibrated pH meter's probe together with the associated temperature probe is immersed in the sample to cover at least 1/3 of the probes whiles stirring with a magnetic stirrer preset at 600 rpm. The

probe detected the hydrogen ion concentration and reports the negative logarithm of the concentration as a pH value. The values obtained were recoreded as the pH values.

#### 3.3.9 Assessment of Odour Emissions

Odour emissions were assessed using the annoyance measurements by Perrin-Koster approach based on population panels, annoyance scale, and filter questions (Koster *et al*, 1985; Perrin *et al*, 1989). A sample is as shown in Appendix 6. A fifty member panel, representative of the population (in terms of age, social status, and dependence on the industry) was recruited from Apimanim No.2, the closest village from GREL's processing factory in the Western Region of Ghana. The panel made their evaluation using a standard form provided after 2 minutes exposure to the gases emitted from the oven's vent. Evaluations were done when drying each of the mechanical pre-treated samples throughout their corresponding maturation periods as set out in the experimental method. Assessments were done independently and the results obtained were analysed with Odour Annoyance Index (O.A.I) calculated as follows:

$$O.A.I = \frac{0N_0 + 0N_1 + 25N_2 + 50N_3 + 75N_4 + 100N_5}{N_{total}}$$
Equation (8)

Where:

 $N_0$ = number of people having responded "no odour"  $N_1$ = number of people having responded "not annoyed"  $N_2$ = number of people having responded a "little bit annoyed"  $N_3$ = number of people having responded "annoyed"  $N_4$ = number of people having responded "very annoyed"  $N_5$  = number of people having responded "extremely annoyed"

In this formula, the O.A.I varies from 0 to 100 and only responses indicating annoying odour are taken into account.



#### **CHAPTER FOUR: RESULTS AND DISCUSSIONS**

Following the experimental and test methods described in Chapter Three, the results and discussions for chemical and mechanical pre-treatments are as presented in section 4.1 and 4.2 respectively.

Sub-section 4.1.1 - 4.1.3 deals with the impacts of the each of the chemicals tried in this experiment on the odour causing compounds (mercaptans). It also explains the consequence of the concentrations of each of the chemicals applied on the rate of utilisation of the carbohydrate materials by the microbes. Sub-section 4.1.4 however explains the effect of all the chemicals tried under the chemical pre-treatment experiments on the final products characteristics.

Sub-section 4.2.1 - 4.2.5 on the other hand, discusses the impact of both mechanical pre-treatment and maturation periods on the product characteristics and odour emission levels.

# 4.1 THE IMPACT OF CHEMICAL PRE-TREATMENT ON LATEX

# CARBOHYDRATES AND MERCAPTANS.

The choice of chemicals for the experiment was based on the objectives of the work. This is because not all the chemicals applied here are currently applied in the rubber industry. Whereas acetic acid, hydroxylamine sulphate and phosphoric acids are used in the NR industry, copper (II) EDTA chelates were only introduced into the work for experimental purposes.

Figure 4.1 Calibration curve for the determination of total carbohydrates



Source: Experimental computation, 2011. (k=1/M=2.127; M= slope of calibration

curve).

Figure 4.2 Calibration curve for the determination of mercaptans



Source: Experimental computation, 2011. (k=1/M=0.1244 is the constant; M= slope of calibration curve).

As indicated earlier, chemical pre-treatments required the determination of total carbohydrates and mercaptans during the course of the fermentation of the latex. Following the spectro-photometric method already described in Chapter 3, two calibration curves were obtained for the determination of total carbohydrates and mercaptans as shown on Fig. 4.1 and Fig. 4.2 respectively.

These curves were therefore used to deduce the actual concentrations of the absorbance readings by the slope of the model equation. All results are as tabulated in Appendix 8(a) and Appendix 8(b) from which Fig. 4.3 - Fig. 4.12 were plotted.

#### 4.1.1 Impact of phosphoric and acetic acids addition to latex

Acetic acid proved to be more efficient than phosphoric acid in terms of its impact on the concentration of mercaptans and carbohydrate materials in the fermenting media upon treatment of latex with the same quantity of each of the acids. From Fig. 4.3 - Fig. 4.4 below, 1% solution of acetic acid applied at the treatment concentrations of 5.3, 6.7, 13.3 g/kg.dry rubber reduced the level of mercaptans present at 0 h in the latex by 27.9%, 28.6%, 69.8% respectively. However when 1% phosphoric acid was applied at the same treatment concentrations (5.3, 6.7, 13.3 g/kg.dry rubber), there was a reduction of 19.3%, 20.7% and 65.4% respectively for mercaptans, using the control treatment (0 g/kg.dry rubber) as the basis. The same effect was also observed with regards to the carbohydrate material. Thus, when acetic acid was applied at the treatment concentrations of 5.3, 6.7 and 13.3 g/kg.dry rubber, there was a reduction of the carbohydrates material available in the latex at 0 h by 46.3%, 39.6% and 49.8%. However, when phosphoric acid was applied at the rate of 5.3, 6.7 and 13.3 g/kg.dry rubber, there was a reduction in the carbohydrates by 15.8%, 24.3% and 43.0% respectively.





Source: Experimental data, 2011.

Figure 4.4 Impact of acetic acid used as coagulant on mercaptans.



Source: Experimental data, 2011.

Secondly, according to Fig. 4.5 and Fig. 4.6 it was observed that, increasing the quantity of acid (from 0.0 to 13.3 g/kg dry rubber) did not inhibit the microbial

conversion of the carbohydrate material present in the fermenting medium. Hence microbial action on the carbohydrates during 0 h to 96 h of fermentation continued leading to the production odorous by-products like mercaptans as indicated on Fig. 4.3 and Fig. 4.4. Thus, microbial action on carbohydrates continued irrespective of the quantity and the type of the acid used. Additionally, the rate of depletion of the carbohydrates form 0 h to 96 h were comparable in between the treatment concentrations of 5.3, 6.7, 13.3 g/kg dry rubber and even with the control (0.0 g/kg. dry rubber) for both acetic and phosphoric acid. This suggests that, for production of latex grades (where coagulation is achieved through acid induced conditions), if the coagulum is not processed immediately after the coagulation as practised currently in the industry, but kept for about 96 hours (as in the case of this experiment), natural fermentation may set in to generate mercaptans and hence the odour.

Figure 4.5 Impact of phosphoric acid as coagulant on latex carbohydrates.



Source: Experimental data, 2011.

Figure 4.6 Impact of acetic acid as coagulant on latex carbohydrates.



Source: Experimental data, 2011.

#### 4.1.2 Impact of copper (II) EDTA chelate added to latex.

Copper (II) EDTA chelate was capable of sequestering most of mercaptans produced in the fermentation medium but inhibited the fermentation-microbes beyond the Cu (II) EDTA treatment concentration of 1.3 g/kg.dry rubber. From Fig. 4.7, increasing the concentration of copper (II) ions resulted in a decrease in the quantity of mercaptans originally (at 0 h) present in the latex. Thus, at Cu (II) EDTA treatment concentrations of 0.7, 1.3, 2.0, 2.7, 3.3 and 4.0 g/kg.dry rubber, there was a reduction of the mercaptans by 45.9%, 57.4%, 60.0%, 62.7%, 66.1%, and 73.1% respectively when compared with the control sample (0.0 g/kg.dry rubber). This affinity of copper (II) ions for mercaptans is in line with the earlier report made by Robert *et al*, (2010). **Figure 4.7** The rate of oxidation of mercaptans with increasing concentration of Cu (II) EDTA chelate.



Source: Experimental computation, 2011.

Though mercaptans levels were lowered from an average of 0.052 m.mol/l for fresh latex to an average of 0.014 m.mol/l at a treatment concentration of 4.0 g/kg dry rubber of copper (II) EDTA, it was observed that, the coagulums formed were still producing a very annoying smell (Koster, 1985). This observation could be explained by the formation of disulphides (Robert *et al*, 2010). Here, the mercaptans were oxidized by Cu (II) in a reaction which led to the loss of mercaptans, measured by its reaction with 5, 5'-dithio-bis (2-nitrobenzoic acid), and formation of Cu (I). That is, Cu (II) reacts with mercaptans to form Cu (II)-mercaptans complexes, Cu (II) is reduced to Cu (I), and the mercaptans are oxidized to the corresponding radicals" which may come together to form disulphides.

Additionally, from Fig. 4.9, it was observed that; at copper (II) EDTA treatment solution concentration of 1.3 g/kg dry rubber, the concentration of the mercaptans diminished from 0.0226 mmol/l at 0 hour to 0.0067 mmol/l at the end of

24 hours. However, it was observed that there was rather an upward trend after 24 hours through the 96<sup>th</sup> hour leading to an increase of mercaptans from 0.0067 mmol/l at 24 hours to 0.0188 m.mol/l at the end of 96<sup>th</sup> hour. This increase in mercaptans level at this concentration (1.3 g/kg dry rubber) beyond 24 hours could be due to yeast producing extra H<sub>2</sub>S and hence mercaptans in response to toxic substances in order to survive and continue the fermentation as long as the substrates are available. This observation is in line with the earlier report by Zoecklein et al (2007). This concentration therefore corresponds to the maximum tolerable concentration beyond which the micro-organisms are inhibited. This suggests that, in between the treatment concentration of 2.0 - 4.0 g/kg dry rubber, the observed reduction in the concentration of mercaptans from the 0 h values to the 96 h values were as a result of diffusion when the microbes were inhibited from producing extra mercaptans as in the case of the treatment concentration of 1.3 g/kg dry rubber. Consequently, from Fig. 4.10, beyond the treatment solution concentration of 1.3 g/kg dry rubber of copper (II) EDTA chelate, it was observed that the rate of utilisation of the carbohydrate materials was greatly reduced. This confirms the inhibition of the microbes which otherwise would have utilised the carbohydrate material if the microbes were not inhibited. Thus, from Fig. 4.10 between 0 h and 24 h, the carbohydrate utilisation rate corresponding to the various treatments concentrations dropped as follows: 90.7%, 68.4%, 51.0%, 35.3% and finally to 32.5% for 1.3, 2.0, 2.7, 3.3 and 4.0 g/kg Cu(II)EDTA treatment concentrations respectively. This trend is as shown on Fig. 4.8. This observation could be explained from the fact that, at 0 h of Fig 4.10, concentration of carbohydrates for all the Cu (II) EDTA treatments did not vary significantly, but beyond the treatment concentration of 1.3 g/kg.dry rubber,

the concentration of carbohydrates in the fermenting media at each of the 24 h kept increasing.

**Figure 4.8** The % change in the concentration of carbohydrates between 0 h and 24 h for latex treated with varied amounts of Copper (II) EDTA chelates.



Source: Experimental computation, 2011.

Figure 4.9 Effect of copper (II) EDTA chelate on mercaptans during fermentation.



Source: Experimental data, 2011.

**Figure 4.10** Effects of copper (II) EDTA chelate on the carbohydrates during fermentation.



Source: Experimental data, 2011.

### 4.1.3 Impact of hydroxylamine sulphate salts (HNS)

Hydroxylamine sulphate could not suppress the level of mercaptans generated during the fermentation stages. It was observed that increasing the concentration of hydroxylamine sulphate (HNS) made little or no impact on the production of mercaptans. Similarly, the addition of hydroxylamine sulphate to latex did not produce any direct correlation between the applied treatment concentrations and the carbohydrates utilisation rate from the latex. **Figure 4.11** The effect of hydroxylamine sulphate on carbohydrates conversion during fermentation.



Source: Experimental data, 2011.

Figure 4.12 The impact of hydroxylamine sulphate (HNS) on mercaptans during latex fermentation.



Source: Experimental data, 2011.

# 4.1.4 Effects of chemical pre-treatment on the physical properties of processed NR.

All the resulting products obtained from the chemical pre-treatments were tested for Wallace plasticity (Po), Plasticity retention index (PRI) and Mooney viscosity. Results are as tabulated in Appendix 9. Based on ISO 2000 norms for the specification and classification of natural rubber (Appendix 10); it was observed that, hydroxylamine neutral sulphate (HNS), acetic and phosphoric improved the product properties, whereas all treatments by Cu(II)EDTA chelate lowered product properties below minimum required levels.

Analysis of the results in Appendix 9 shows that, acetic acid, phosphoric acid, and hydroxylamine sulphate caused an increase in the PRI of the resulting products whereas copper (II) EDTA degraded the PRI. The impacts of these chemicals on PRI, Po, and Mooney viscosity are as shown on Fig. 4.13- Fig. 4.16.

In terms of Mooney viscosity and Wallace plasticity, whilst HNS caused a slight reduction in the Mooney viscosity and Wallace plasticity, the two acid coagulants tried here (acetic and phosphoric) also caused a slight increase in the Mooney viscosity and Wallace plasticity when compared with the control treatment sample (Fig. 4.14.- Fig. 41.6). Despite these slight modifications of the product properties by the acid coagulants and HNS, all product properties were within the acceptable range in the ISO 2000 requirements.

Although acetic acid, phosphoric acid and HNS were satisfactory in terms of their impact on the product properties, all of them were less effective in mitigating mercaptans-odour when compared with copper (II) EDTA chelates treatments as already explained. However, from Fig. 41.3, each of the relatively low treatment concentrations (from 0.7 to 4.0 g/kg. dry rubber) of the Copper (II) EDTA degraded the product woefully beyond the minimum required levels (ISO 2000) for each of the properties, when compared with the treatment concentrations of the other chemicals.

Figure 4.13 Impacts of Cu (II) EDTA chelates treatments of latex on dry NR properties



Source: Experimental computation, 2011.

Figure 4.14 Impacts of phosphoric acid treatments of latex on dry NR properties.



Source: Experimental computation, 2011.

Figure 4.15 Impacts of acetic acid treatments of latex on dry NR properties.



Source: Experimental computation, 2011.

Figure 4.16 Impacts of HNS treatments of latex on dry NR properties.



Source: Experimental computation, 2011.

# 4.2 THE IMPACT OF MECHANICAL PRE-TREATMENT AND MATURATION ON PRODUCT CHARACTERISTICS AND PROCESS-ODOUR EMISSIONS.

#### 4.2.1 The impact of mechanical pre-treatment on heat degradation rate.

All products obtained from the five different processes of pre-treatments (Agglomerated, Free cuplumps, Slab-cut, Macerated and Crept blankets) were allowed to mature separately for a total of four weeks (672 h). Portions of each of the five pre-treated lots were taken, processed and were tested every week (168 h) using accelerated heat ageing test. The results of the plasticity after accelerated ageing tests are as tabulated in Appendix 11. The natural logarithm of each of the aged plasticities in Appendix 11 was calculated as shown in Appendix 12. A plot of the logarithm of the Wallace plasticities after ageing versus the ageing time for each samples at a specific maturation period and the associated phosphoric acid treatment resulted in a heat degradation models. Examples are as shown on Fig. 4.17 - Fig. 4.21.

It was observed from the plots that the heat degradation of all samples obtained from the experiment, irrespective of the pre-treatment process of maturation period observed obeyed first order kinetics. However, each sample exhibited a specific degradation rate constant, k determined from the slope of the linear model as displayed on Fig. 4.17 – Fig. 4.21 for 0% phosphoric acid treatments and in Appendix12(b) for both 1% and 2% phosphoric acid treatments. This observation agrees with data obtained elsewhere (Sambhi, 1989). The degradation constants obtained in this work are as summarised in Appendix 13. The results show that, rubber produced from the bulk sample at maturation period equals 0 h (without any
phosphoric acid treatment), had a degradation constant of  $-0.024 min^{-1}$ . The degradation rate constant, *k* of each of the samples changed from the 0 h value  $(-0.024 min^{-1})$  depending on the type of pre-treatment, maturation period or the concentration of phosphoric acid used (refer to Appendix 13 for details).

**Figure 4.17** Plot of ln(P) versus ageing time for cuplumps processed at 0 h maturation without phosphoric acid crumb treatment.



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Source: Experimental computation, 2011.

**Figure 4.18** Plot of ln(P) versus ageing time for processed cuplumps initially subjected to varied pre-treatments and a maturation period of 168 h, without phosphoric acid treatment.



Source: Experimental computation, 2011.

**Figure 4.19** Plot of ln(P) versus ageing time for processed cuplumps initially subjected to varied pre-treatments and a maturation period of 336 h, without phosphoric acid treatment.



Source: Experimental computation, 2011.

**Figure 4.20** Plot of ln(P) versus ageing time for processed cuplumps initially subjected to varied pre-treatments and a maturation period of 504 h, without phosphoric acid treatment.



Source: Experimental computation, 2011.

**Figure 4.21** Plot of ln(P) versus ageing time for processed cuplumps initially subjected to varied pre-treatments and a maturation period of 672 h, without phosphoric acid treatment.



Source: Experimental computation, 2011.

Generally, it was observed that mechanical pre-treatment processes that results in crept blankets gave the lowest degradation rate constants, followed by the macerated. This suggest that the amount of non-isoprene constituents extracted (Appendix 15) from the materials before maturation impacts on the heat degradation behaviour of the material after processing.

# 4.2.2 Impact of mechanical pre-treatment on degradability of natural rubber properties during maturation.

Maturation storage of mechanically pre-treated cuplumps causes chainscissions (as seen in reduction in Wallace plasticity); or cross-linking (which results in an increased in Wallace plasticity) of the polyisoprene chains, depending on the combined effect of pre-treatment process employed and maturation period. Detailed results of plasticity for each dried pre-treated material with their corresponding maturation periods are as presented in Appendix 14.

A plot of plasticities of samples whose crumbs were treated with 0% phosphoric acid during processing is as shown on Fig. 4.22. From the Fig. 4.22, there was a general reduction in the Wallace plasticity (Po) of each pre-treated sample produced at a maturation period of 168 h when compared with the Wallace plasticities recorded as at 0 h maturation. However, the extent of the reduction in Wallace plasticity of each sample depends on the kind of mechanical pre-treatment process used. Thus from Fig. 4.22, there was a reduction in Wallace plasticity by 25.0%, 25.0%, 27.1%, 1.9% for Agglomerated, Free cuplumps, Slab-cut, Macerated samples respectively; whereas there was a gain of 0.4% crept blankets between a maturation period of 0h to 168h. This observation is in line with the common knowledge that, microbes live at the expense of their substrates when other growth

factors are available. Thus, natural microorganisms present in latex coagula lived and survived at the expense of the non-rubber constituents made up of proteins, carbohydrates, lipids, and inorganic salts (Subramaniam, 1995) and the rubber hydrocarbon itself (Linos, 2000) leading to biodegradation. Therefore any maturation period observed before processing corresponds to a degree to which the microbial activities have proceeded using both the isoprene and the non-isoprene components as substrates whilst the kind of mechanical pre-treatment method/equipment impacted on the extent to which the non-rubber fraction (Tuampoemsab, 2008) were removed before the start of the maturation period. The extent of removal of the components of the non-rubber fraction by each mechanical pre-treatment process is as shown in Appendix 15.

The observed reduction of the Wallace plasticity as a result of maturation is in line with the hypothesis proposed by Tsuchii *et al* (1985) that microbes are responsible for the degradation via the oxidative scission of the cis-1,4-double bond as the primary step in biodegradation of the cis-1,4-polyisoprene chain leading to lowering of the Wallace plasticities of NR.

However, from Fig. 4.22, beyond 168h of maturation, there was an increase in Wallace plasticity for all pre-treatment methods employed in this experiment due to cross-linking. This observation is also in line with submissions made by earlier workers (Burfield, 1974; Subramaniam, 1976, 1977, 1984; and Eng *et al*, 1994). Accordingly, the change in the properties of NR during storage is presumed to be due to the cumulative effect of both cross-linking and chain-scission (Nimpaiboon, 2009), which also depends also on the availability of other non-rubber constituents such as proteins molecules or free amino acids and the aldehyde groups present on the rubber molecules itself (Subramaniam, 1984).

**Figure 4.22** The change in Wallace plasticity of products obtained from the different pre-treatments during maturation, with 0% phosphoric acid treatment during processing.



Source: Experimental computation, 2011.

# 4.2.3 Impact of mechanical pre-treatment and maturation on physical properties of processed NR.

Products obtained just after processing each sample from the experiment was immediately tested for Po, PRI, Colour and Mooney Viscosity. Initial Wallace plasticity (Po) is generally controlled by the net effect of cross-linking and chainscissions and their values depend on both the period of maturation and the pretreatment equipment as shown in Fig. 4.22.

PRI values determined by ISO2930:2009 were another very important parameter observed (Appendix 16). Plots of the PRI values obtained during maturation for each of the pre-treated materials are as shown on Fig. 4.23 – Fig. 4.25.

It was observed that the PRI was controlled by pre-treatment process (equipment involved) and maturation period as well. This observation agrees with earlier reports made by Tuampoemsab (2007) that non-rubber components influence the heat-ageing behavior of natural rubber. That is, the extent of non-rubber components removal by the different pre-treatment processes (Appendix 15) employed in this experiment correlates well with the PRI values. Thus, PRI increased proportionally to the extent of non-rubber removal caused by the pre-treatment process as depicted on Fig. 4.23 – Fig. 4.25 below.

Generally it was observed that crept blankets gave a superior product followed by the macerated in terms of PRI. All the other treatments were not significantly different from each other during maturation (refer to Appendix 22; calculated values of F were all less than the critical values, *Fcrit*).

**Figure 4.23** The change in PRI of NR produced from different pre-treatments during maturation (crumbs sprayed with 0% phosphoric acid during processing).



Source: Experimental computation, 2011.

**Figure 4.24** The change in PRI of NR produced from different pre-treatments during maturation (crumbs sprayed with 1% phosphoric acid during processing).



Source: Experimental computation, 2011.

**Figure 4.25** The change in PRI of NR produced from different pre-treatments during maturation (crumbs sprayed with 2% phosphoric acid during processing).



Source: Experimental computation, 2011.

Another remarkable observation in the experiment was the resulting colour (Lovibond, ISO 4660) of the products gotten from the different pre-treatment and maturation periods. Generally, macerated and crept blankets pre-treated materials produced darker or "less light" rubber than the other modes of pre-treatment. The intensity of the darkness also depended on the length of the maturation period. The analytical results are as shown in Appendix 17.

Furthermore, Mooney viscosity observed during the experiments were closely related to the Wallace plasticities as indicated elsewhere (Internal ASTM interlab Crosscheck for D3184). Details are provided in Appendix 18.

# 4.2.4 The impact of mechanical pre-treatment and maturation on phosphoric acid consumption during processing.

With regards to the Molybdate method applied for the determination of the concentration of phosphoric acid solutions, a calibration curve was derived to test for the concentration of phosphoric acid solution used in spraying rubber crumbs. Calibration curve is as shown on Fig. 4.26 below.

It is a common knowledge in the natural rubber industry that, treatment of shredded rubber crumbs with phosphoric acid solutions prior to drying, results in increase in PRI and consumption of phosphoric acid over time.

Though, it was observed that, all samples obtained from the different combinations of mechanical pre-treatment and maturation tried here gave comparable phosphoric acid consumption (Appendix 19), the response of each of the pre-treated samples to phosphoric acid varied depending on the pre-treatment process, maturation period and concentration of phosphoric acid.

**Figure 4.26** Calibration curve for the determination of %phosphoric acid by Molybdate method at 410 nm.



Source: Experimental computation, 2011. (k=1/M is the constant; M= slope of calibration curve).

The response of each of the samples to phosphoric acid treatments, expressed in terms of PRI, is as displayed in Appendix 16. From Appendix 16, the gain in PRI comparing zero (0%) phosphoric acid treatment and 2% treatments are as summarised in **Tab. 4.1** below.

 Table 4.1 Comparative data on gain in PRI values from NR crumbs treated with 0% and 2% phosphoric acid.

	0 h	168 h	336 h	504 h	672 h
Agglomerated	7.9	5.3	6.9	6.0	4.9
Free cuplumps	7.9	4.2	4.9	5.7	4.0
Slab-cut	7.9	5.9	5.0	7.5	5.9
Macerated	7.9	12.5	3.0	2.3	3.4
Crept blankets	7.9	12.0	2.2	0.8	-1.8

Source: Experimental data, 2011.

PRI gains obtained through phosphoric acid for Agglomerated, Freecuplumps and Slab-cut cuplumps from 0 h through 504 h ranges from PRI values between 4.2 and 7.9. This observation is consistent with the industrial standards. However, it was observed that beyond a maturation period of 336 h, phosphoric acid had negligible effect on both crept blankets and macerated samples. Specifically, beyond 336 h of maturation, even 2% phosphoric acid treatment resulted in an average increase in PRI by 2.3% ( at 504 h) and 3.4% ( at 672 h) for macerated samples. Crept blankets however gained just 0.8%, at 504 h, and recorded

-0.8% at 672 h. With regards to precision of the measuring instrument used in this work (Wallace Plastimeter,  $\pm 0.5$ ), there was no significant increase in the PRI of the 0% and the 2% phosphoric acid treatment for the crept blanket samples at both 504 h and 672 h.

Hence, with regards to the requirement for grading and specification under ISO 2000, and the results obtained in this experiment, it was observed that phosphoric acid spraying could be avoided based on the choice of pre-treatment and maturation period adopted.

# 4.2.5 Impact of mechanical pre-treatment and maturation on odorous gas emissions.

Odour annoyance index (O. A. I) evaluation was performed on data obtained using Perrin-Koster Approach (Koster *et al*, 1985; Perrin *et al*, 1989) from the panel of fifty people. The result is as captured under Appendix 20 and summarised in Tab. 4.2. It was observed that for all pre-treatment operations after 0 h maturation, odour levels was highest with the control samples and reduced depending on the extent to which the process extracted the non-isoprene (non- rubber) constituents. Thus odour level was highest with the agglomerated and the free cuplumps and least with the crept-blanket sample as shown below.

 Table 4.2 Odour Annoyance Indices of pre-treated samples during drying with

 varied maturation periods.

Rubber	Odour Annoyance Index (at a maturation period)				
Sample	0 h	168 h	336 h	504 h	672 h
Agglomerated	71.5	80.0	73.5	72.0	72.0
Free cuplumps	71.5	74.5	63.5	74.5	75.0
Slab-cut	71.5	73.0	60.5	74.5	65.5
Macerated	71.5	65.0	42.0	24.5	21.0
Crept blankets	71.5	47.0	24.5	2.5	1.0

Source: Experimental computation, 2011.



#### **CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS**

#### **5.1 CONCLUSION**

With due consideration to the objectives of this work, the experimental methods used and results obtained so far, the following conclusions can be drawn. First, with regards to chemical pre-treatments of latex, it can be concluded that; phosphoric and acetic acids used as coagulants of latex had very little impact on suppressing the mercaptans odour produced on cuplumps-grade process, notwithstanding the fact that these acids impacted positively on the final product's PRI as discussed earlier.

Secondly, the addition of hydroxylamine neutral sulphate to latex cannot serve the purpose of mitigating the fermentation odours caused by mercaptans. Thus, for all concentrations tried in this work, hydroxylamine sulphate did not impact on the rate at which latex carbohydrates were utilised by micro-organisms. Neither was increasing the concentration of hydroxylamine sulphate increased its potential to inhibit or sequester mercaptans that were generated in the process of fermentation. However, hydroxylamine reduced the products Mooney viscosity- in line with its present use in the rubber industry.

Furthermore, the various solutions of copper (II) EDTA chelates were much more effective against mercaptans but had an oxidising effect on the product itself as well. Thus, mercaptan odours were suppressed by copper (II) EDTA chelate at the expense of product quality expressed through lowering the Wallace plasticity, Plasticity retention index and Mooney viscosity. Thus, Cu (II) EDTA chelates rendered the products out-of specification because resulting products had Wallace plasticities and PRI that were below the minimum required under ISO2000 standard. The unsatisfactory results obtained from the chemical pre-treatment makes all the chemical pre-treatment tried here insufficient for mitigating odour in a natural rubber processing environment.

On the other hand, mechanical pre-treatment caused an improvement in most of the critical physical properties of NR but the extent of improvement is proportional to the extent to which non-isoprene (non-rubber) constituents were extracted from the cuplumps during pre-treatment operations. Thus, crept blankets and macerated gave a much improved material in terms of PRI in the course of the maturation period. Though their colours (Lovibond) were quite darker, all other technological parameters such as PRI, Wallace plasticities, Mooney viscosities, heat degradation rate and even odour annoyance levels from gases emitted from the dryers improved.

From the experimental method and the results obtained so far, best unit equipment in mechanical pre-treatment of cuplumps is through the use of a pretreatment process that includes the seven (7) serially arranged crepers that shear the material into blankets before maturation. Thus, crept blankets performed creditably between 168 h though the 672 h of maturation in terms of resistance to heat degradation, Wallace plasticity (Po), Plasticity retention index (PRI), and more importantly emitted the least annoying smell during drying.

From the results obtained, the optimum maturation period is at 504 h (21 days) after pre-treatment. This is because, 504 h of maturation period corresponds to a point at which all the material properties like Wallace plasticity, Mooney viscosity and Plasticity retention index are optimised (refer to results in Chapter Three)

An environmentally friendly model of rubber processing is the one which reduces phosphoric acid consumption and mitigate odour emission. It can be deduced from this work that, the environmentally friendly process is the crept blankets pre-treatment process in addition to a maturation period of 504 h (21days). It has been shown at Appendix 16 and Tab 4.2 that, the gain in PRI by spraying crept blankets with 1% to 2% phosphoric acid did not make a significant impact on the product PRI when compared with the 0% phosphoric acid treatment after 336 h of maturation.

This study therefore concludes that, there is the possibility to mitigate NR odours emitted by factories, improve product characteristics and reduce or avoid phosphoric acid consumption. There is therefore the need to conduct a feasibility study for the design of new factories in which the wet-line could be used as a pre-treatment line, to maturation storage, then to shredder, before the dry-end follows; with the objective of optimising energy use, reduction in phosphoric acid usage, improved product characteristics and odour mitigated. Refer to Appendix 21 for proposed long term configurations.

#### 5.2 SUGGESTIONS FOR FURTHER WORK

Based on the results obtained through this work, the author would like to suggest the following for further studies:

 To identify the family of the micro-organisms present on each group of mechanical pre-treated samples during the maturation period of 0 h - 672 h to reduce the optimum maturation from 504 h (21days) to about 168 h (7days). 2. To analyse the gases released during drying by GC-MS to ascertain the chemical composition of the gases released from each of the samples for comparative study.



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# APPENDIX 1: Properties of NR and Synthetic IR polymerised with Ti-Al and

## Li catalyst

	Property	NR	IR(Ti-Al)	IR(Li)
1.	Cold flow	Excellent	Excellent	Good
2.	Green strength	Excellent	Poor	Worst
3	Green tack	Excellent	Excellent	Excellent
4	Role processability	Excellent	Excellent	Good
5	Injection processability	Excellent	2	
6	Press processability	Excellent	Excellent	Excellent
7	Calendar processability	Excellent	Excellent	Good
8	Vulcanisation rate	Excellent	Excellent	Good
9	Tensile strength	~320	~300	~280
10	Tear strength	Excellent	Good	Good
11	Resilience	Excellent	Excellent	Excellent
13	Abrasion	Good	Good	Good
15	Chipping	Good/Excellent	Good	Poor
16	Cutting	Good/Excellent	Good	Poor

Source: Mark et al, 1998.

## **APPENDIX 2(a): Process flow for latex grade line**





### **APPENDIX 2(b): Process flow chart for field/cuplumps grade production**

### **APPENDIX 3:** Sample calculations for treatment of latex with HNS.

- The latex has an estimated dry rubber content of 30%. Therefore, for 250g latex, the dry rubber content equals = 0.075 kg
- Therefore by proportion, to treat latex to achieve the HNS concentration in the mixture to be 1g HNS / kg. dry rubber; we needed 0.075 g of HNS.
- Therefore, in order to prepare 1% solution of HNS before adding to the latex,
   0.075g of HNS was weighed and diluted in 7.5 ml of distilled water before adding to the 250g of latex.
- To achieve a latex-HNS mixture whose concentrations of HNS is 1.5 g/kg dry rubber and 2.0g/kg dry rubber, 0.1125 g and 0.15 g of HNS were weighed respectively.
- The 0.1125 g and the 0.15 g weighed were each diluted with 11.2 l and 15.0 l of distilled water before addition into their respective 250 g of latex.



#### APPENDIX 4: Sample calculations for treatment of latex with 1% acetic acid

- Firstly, the burette was filled with 1% solution of acetic acid.
- 250 g latex was the weighed and placed under the burette containing the acid coagulant (1% acetic acid).
- A calibrated pH meter was then placed in the latex.
- The 1% acetic acid was released into the latex whilst stirring until the pH of the solution was 5.2, which is the recommended pH for coagulation.
- This corresponded to 40 ml of acid released from the burette.
- Other two treatments of latex used 50 ml and 100 ml respectively.
- The concentration of the acid in the mixture was calculated as follows:
  - > 40 ml of 1% acetic acid was assumed to have the same density as the distilled water used in the preparation of the solution.
  - > 40 ml of the 1% acetic acid contains, 0.4g of pure acetic acid
  - 50 ml and 100 ml of the 1% acetic also contain 0.5 g and 1 g of the pure acid respectively.
  - The latex had a dry rubber content of 30%, which means for each 250g of latex, the dry rubber content was 0.075kg.
  - Therefore the concentrations of the acid applied in 250 g latex (equivalent to 0.075 kg dry rubber) are as tabulated in Tab. AP 4/1 below.
  - The same computation was done when phosphoric acid was used as acid coagulant. However, the quantity of 1% phosphoric acid that gave a pH of 5.2 was 100 ml.
  - However, 40 ml of the acid was added to 250 g latex, and 50 ml of the acid was also added separately to another 250 g latex comparative analysis.

## **APPENDIX 4: Sample calculations for treatment of latex with 1% acetic acid**

# (continued).

Table AP 4/1 concentration of pure acids used in coagulating latex.

Sample label	Quantity of pure	Concentration
	acid, g	of acetic acid
		used, g/kg.dry
	KNI	rubber
40 ml	0.4	5.3
50 ml	0.5	6.7
100 ml	1.0	13.3



### **APPENDIX 5:** Sample calculations for treatment of latex with copper (II)

### **EDTA chelate.**

- Seven pieces of clean 50 ml capacity conical flasks were picked and label the A 0 to G.
- The quantity of copper(II)EDTA chelate weighed into each of the flasks are as 0 shown on Table AP 5/1 below:

.

/ II Table AP 5/1 quantities of copper (II) EDTA required to prepare each solution.

oper(II)EDTA, g 0.0 0.5
0.0 0.5
0.5
1.0
1.5
2.0
2.5
2.0
3.0

- 10 ml of distilled water was added to each of the flask containing the copper (II) 0 EDTA and stirred each on a magnetic stirrer for 5 minutes until complete dissolution was achieved.
- o 250 g of latex was into each of a seven different latex cups, labelled A to G.

# APPENDIX 5: Sample calculations for treatment of latex with copper (II) EDTA chelate (continued).

- With reference to the labels on the solutions and the latex in the cups, 1 ml of prepared solution was added to the latex in the cups correspondingly.
- This produced latex whose concentration copper (II) EDTA in the mixture were as displayed on Table AP 5/2 below.

J

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Table AP 5/2 concentration of copper (II) EDTA in each latex mixture.

**N** 

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Sample label	Concentration of	Concentration of	Concentration of
	Copper(II)EDTA	Copper(II)EDTA	Copper(II)EDTA
	in latex, g/g.latex	in latex, mg/g.latex	in latex, g/kg dry
			rubber
A	0.0000	0.0	0.0
В	0.0002	0.2	0.7
С	0.0004	0.4	1.3
D	0.0006	0.6	2.0
E	0.0008	0.8	2.7
F	0.0010	1.0	3.3
G	0.0012	1.2	4.0
#### **APPENDIX 6: Machines used for mechanical pre-treatment**

MACHINE	CHARACTERISTICS
1. Slab cutter	1) Output= 12-15ton/h
(helically arranged knives mounted on a rotating	2) Gap between knives and combs.
shaft. knives shearing rubber across two	2.1) between upper combs and knives =2.5 cm
stationary combs)	2.2) between lower combs and knives=3.0 cm
	3) Motor=45 kW, 1500 rpm,
	4) Reducer=30 : 1



MACHINE	CHARACTERISTICS
1. Macerator (Coarse creper)	1) Rated output= 4 -5 ton/h
(two toothed roll-mill with special grooves)	2) Roller size
	2.1 ) length = 76 cm
	2.2 ) diameter=41cm
	3) gap/nip between rollers=1.0 mm
19	4) Roller grooves:
	4.1) diagonals of parallelogram= $17.6 \text{ mm} \times 25 \text{ mm}$
T	4.2) depth of groove = 4.0 mm $\pm$ 0.1mm
Capacity	5) Motor:45 kW; 1500 rpm
	6) Reducer 30:1

#### **APPENDIX 6: Machines used for mechanical pre-treatment (continued)**

#### **APPENDIX 6: Machines used for mechanical pre-treatment (continued)**

MACHINE	CHARACTERISTICS
1. 7 serially arranged crepers made up of	1) Rated output= $4-5 \text{ ton/h}$
2coarse, 3medium and 2half smooth	2) Roller size: <i>length</i> = 76 <i>cm</i> , <i>diameter</i> =41 <i>cm</i>
(two toothed roll-mill with special grooves)	3) gap/nip between rollers: Coarse= 0.4 mm; medium= 0.2 mm;
	half-smooth= 0.05 mm
	4) Roller grooves:
	4.1) Diagonals of parallelogram = $17.6 \text{ mm} \times 25 \text{ mm}$ for all.
	4.2) depth of grooves=
HT I	✓ coarse: 4.0 mm± 0.1 mm
COPS COPS	✓ medium: 3 mm± 0.1 mm
	half-smooth: $2 mm \pm 0.1 mm$
	5) Motor:45 kW, 1500 rpm
	6) Reducer 30:1

**APPENDIX 7: Odour annoyance evaluation form.** 

Name: . Date:	Ref No:
Sample	
draw up industry	a plan to mitigate the odour nuisance generated by the rubber
Kindly J	position yourself close to the exhaust of the oven as directed.
Wait for appropr	2 2 minutes before the start of the evaluation. Kindly tick the iate box.
Wait for appropr	Do you smell anything at all? yes no

	Application	0	h	24	h	48	3 h	72	2 h	96 h		
Chemical used	rate	Mean	s.e									
Phosphoric Acid	0.0	0.279	0.056	0.053	0.003	0.047	0.005	0.042	0.005	0.027	0.002	
(g/kg, dry rubber)	5.3	0.235	0.056	0.041	0.002	0.041	0.002	0.042	0.003	0.024	0.003	
	6.7	0.211	0.044	0.040	0.001	0.044	0.002	0.041	0.002	0.026	0.002	
	13.3	0.159	0.009	0.035	0.001	0.115	0.002	0.037	0.004	0.016	0.001	
Acetic acid	0.0	0.279	0.056	0.053	0.003	0.047	0.005	0.042	0.005	0.027	0.002	
(g/kg. dry rubber)	5.3	0.150	0.010	0.051	0.001	0.061	0.004	0.063	0.005	0.070	0.005	
	6.7	0.168	0.007	0.040	0.001	0.016	0.002	0.059	0.002	0.061	0.006	
	13.3	0.140	0.004	0.060	0.003	0.060	0.004	0.040	0.003	0.040	0.003	
Hydroxylamine-	0.0	0.279	0.056	0.053	0.003	0.047	0.005	0.042	0.005	0.027	0.002	
Sulphate	1.0	0.288	0.005	0.053	0.001	0.049	0.005	0.078	0.003	0.059	0.006	
(g/kg. dry rubber)	1.5	0.275	0.004	0.118	0.001	0.023	0.004	0.056	0.003	0.070	0.004	
	2.0	0.274	0.006	0.138	0.003	0.051	0.005	0.066	0.004	0.083	0.006	
Cu(II)EDTA chelate	0.0	0.279	0.056	0.053	0.003	0.047	0.005	0.042	0.005	0.027	0.002	
(g/kg. dry rubber)	0.7	0.311	0.007	0.030	0.003	0.038	0.006	0.035	0.005	0.030	0.003	
	1.3	0.321	0.007	0.030	0.002	0.046	0.005	0.036	0.001	0.032	0.003	
	2.0	0.317	0.007	0.100	0.006	0.060	0.005	0.041	0.005	0.040	0.003	
	2.7	0.306	0.003	0.150	0.003	0.078	0.004	0.056	0.005	0.078	0.003	
	3.3	0.309	0.005	0.200	0.006	0.115	0.001	0.100	0.006	0.097	0.004	
	4.0	0.326	0.007	0.220	0.004	0.200	0.003	0.185	0.005	0.150	0.001	

APPENDIX 8 (a): Results of carbohydrates in chemical pre-treated samples in the course of latex fermentation

	Application	0	h	24	h h	<b>GT</b> 48	3 h	72	2 h	96 h		
Chemical used	rate	Mean	s.e	Mean	s.e	Mean	s.e	Mean	s.e	Mean	s.e	
Phosphoric Acid	0.0	0.053	0.0008	0.0241	0.0013	0.023	0.0012	0.019	0.0007	0.010	0.001	
(g/kg, dry rubber)	5.3	0.043	0.0009	0.0174	0.0006	0.020	0.0010	0.020	0.0012	0.013	0.001	
	6.7	0.042	0.0008	0.0151	0.0004	0.020	0.0010	0.028	0.0005	0.014	0.001	
	13.3	0.018	0.0007	0.0086	0.0004	0.033	0.0017	0.016	0.0004	0.011	0.0007	
Acetic acid	0.0	0.0530	0.0008	0.0241	0.0013	0.0230	0.0012	0.0188	0.0007	0.0103	0.0006	
(g/kg. dry rubber)	5.3	0.0382	0.0007	0.0083	0.0005	0.0158	0.0008	0.0189	0.0005	0.0200	0.0006	
	6.7	0.0378	0.0004	0.0083	0.0006	0.0158	0.0008	0.0231	0.0007	0.0200	0.0006	
	13.3	0.0160	0.0005	0.0080	0.0006	0.0120	0.0006	0.0120	0.0005	0.0080	0.0006	
Hydroxylamine	0.0	0.0530	0.0008	0.0241	0.0013	0.0230	0.0012	0.0188	0.0007	0.0103	0.0006	
sulphate	1.0	0.0459	0.0005	0.0212	0.0005	0.0156	0.0008	0.0364	0.0002	0.0139	0.0005	
(g/kg. dry rubber)	1.5	0.0510	0.0010	0.0221	0.0004	0.0112	0.0006	0.0116	0.0004	0.0124	0.0007	
	2.0	0.0513	0.0006	0.0266	0.0006	0.0111	0.0006	0.0111	0.0004	0.0140	0.0005	
Cu(II)EDTA	0.0	0.0530	0.0008	0.0241	0.0013	0.0230	0.0014	0.0188	0.0007	0.0103	0.0006	
(g/kg. dry rubber)	0.7	0.0286	0.0049	0.0129	0.0009	0.0146	0.0011	0.0149	0.0057	0.0141	0.0007	
	1.3	0.0226	0.0050	0.0067	0.0006	0.0137	0.0016	0.0118	0.0077	0.0188	0.0024	
	2.0	0.0212	0.0060	0.0070	0.0006	0.0100	0.0024	0.0100	0.0041	0.0100	0.0013	
	2.7	0.0197	0.0059	0.0074	0.0006	0.0072	0.0011	0.0060	0.0020	0.0050	0.0009	
	3.3	0.0180	0.0034	0.0080	0.0006	0.0060	0.0008	0.0040	0.0012	0.0030	0.0007	
	4.0	0.0142	0.0044	0.0060	0.0006	0.0050	0.0010	0.0050	0.0012	0.0030	0.0005	

Appendix 8 (b): Results of mercaptans in chemical pre-treated samples in the course of latex fermentation

		P	0.				. ML
		(1/100	D)mm	Р	RI, %	(1	+4)
		mean	s.d	mea	n s.d	mean	s.d
Control sample							
(g/kg.dry rubber)	0.0	48.5	0.6	49.7	2.7	85.5	1.0
	0.7	17.7	1.5	17.0	) 3.2	41.0	1.2
Cu(II)EDTA chelate	1.3	12.8	1.2	18.2	2 3.0	10.0	1.4
(g/kg. dry rubber)	2.0	10.7	0.6	20.9	2.8	7.0	1.2
	0.8	10.7	1.5	37.5	5 3.6	18.0	1.6
	1.0	12.0	3.6	36.1	6.2	22.0	2.0
	1.2	9.0	1.0	13.0	) 2.5	11.0	1.2
Acetic acid	5.3*	<mark>54.</mark> 8	0.6	63.8	3 0.3	93.0	0.6
(g/kg. dry rubber)	6.7	52.5	1.2	64.5	5 1.8	90.0	1.5
	13.3	50.0	1.5	67.4	1.4	87.0	1.8
Phosphoric acid	5.3	55.0	1.0	65.0	) 2.5	94.0	1.2
(g/kg. dry rubber)	6.7	55.1	1.5	66.3	3 2.0	93.5	0.8
	13.3*	53.2	1.0	68.5	5 2.4	90.5	1.3
Hydroxylamine	1.0	45.3	1.3	63.5	1.5	84.0	1.5
sulphate	1.5	44.1	0.8	60.4	1.0	80.0	1.0
(g/kg. dry rubber)	2.0	43.0	0.9	64.2	2 1.3	78.0	1.3

#### **APPENDIX 9:** Physical properties of NR obtained through chemical pretreatment.

Source: Experimental data, 2011.

\*quantity of 1% acid needed to reach the required coagulation pH=5.2



## APPENDIX 10: ISO 2000: 1989(E): Standards for specification of natural rubber

Characteristic	Limit	5L	TSR10	TRS20	TSR50
Dirt content, %(m/m) retained on a	Max	0.05	0.1	0.2	0.5
45μm sieve					
Plasticity, (1/100)mm	Min	30	30	30	30
Plasticity Retention Index, %	Min	60	50	40	30
Nitrogen content, % (m/m)	Max	0.6	0.6	0.6	0.6
Volatile matter, w/w%	Max	0.8	0.8	0.8	0.8
Ash,% (m/m)	Max	0.6	0.75	1.0	1.5
Colour Index	Max	6	-	-	-
Mooney Viscosity, ML(1+4)		1	-	7	-

Where:

Max- maximum requirements

Min- minimum requirements

THE COLOR

			0 min		5 m	5 min		10 min		15 min		nin	25 min		30 n	nin
Pre-treatment	Maturation	[H3PO4],					9									
type	period, h	%	Mean	s.e	Mean	s.e	Mean	s.e	Mean	s.e	Mean	s.e	Mean	s.e	Mean	s.e
Agglomerated	0	0	44.7	0.5	42.3	1.3	39.3	1.2	35.5	0.9	30.5	1.0	26.3	0.9	21.8	0.9
Free cuplumps	0	0	44.7	0.5	42.3	1.3	39.3	1.2	35.5	0.9	30.5	1.0	26.3	0.9	21.8	0.9
Slab cut	0	0	44.7	0.5	42.3	1.3	39.3	1.2	35.5	0.9	30.5	1.0	26.3	0.9	21.8	0.9
Macerated	0	0	44.7	0.5	42.3	1.3	39.3	1.2	35.5	0.9	30.5	1.0	26.3	0.9	21.8	0.9
Crept blanket	0	0	44.7	0.5	42.3	1.3	39.3	1.2	35.5	0.9	30.5	1.0	26.3	0.9	21.8	0.9
Agglomerated	0	1	44.8	1.0	42.0	0.9	38.9	1.2	35.5	1.0	31.1	1.3	27.3	1.3	22.8	1.1
Free cuplumps	0	1	44.8	1.0	42.0	0.9	38.9	1.2	35.5	1.0	31.1	1.3	27.3	1.3	22.8	1.1
Slab cut	0	1	44.8	1.0	42.0	0.9	38.9	1.2	35.5	1.0	31.1	1.3	27.3	1.3	22.8	1.1
Macerated	0	1	44.8	1.0	42.0	0.9	38.9	1.2	35.5	1.0	31.1	1.3	27.3	1.3	22.8	1.1
Crept blanket	0	1	44.8	1.0	42.0	0.9	38.9	1.2	35.5	1.0	31.1	1.3	27.3	1.3	22.8	1.1
Agglomerated	0	2	44.2	0.5	42.3	1.0	39.0	1.1	37.1	1.1	32.5	1.1	29.1	1.1	25.0	1.1
Free cuplumps	0	2	44.2	0.5	42.3	1.0	39.0	1.1	37.1	1.1	32.5	1.1	29.1	1.1	25.0	1.1
Slab cut	0	2	44.2	0.5	42.3	1.0	39.0	1.1	37.1	1.1	32.5	1.1	29.1	1.1	25.0	1.1
Macerated	0	2	44.2	0.5	42.3	1.0	39.0	1.1	37.1	1.1	32.5	1.1	29.1	1.1	25.0	1.1
Crept blanket	0	2	44.2	0.5	42.3	1.0	<b>39.0</b>	1.1	37.1	1.1	32.5	1.1	29.1	1.1	25.0	1.1
Agglomerated	168	0	33.5	3.2	28.7	3.4	22.9	3.1	17.2	2.7	12.8	1.4	8.9	1.1	6.0	0.8
Free cuplumps	168	0	33.5	1.2	28.8	0.6	22.7	0.7	16.4	0.9	12.0	1.1	8.2	0.9	5.5	0.5
Slab cut	168	0	32.6	1.0	28.4	2.0	22.6	1.3	16.0	1.2	11.3	0.6	7.4	0.4	4.8	0.3
Macerated	168	0	43.8	1.6	41.5	1.7	38.8	1.9	35.8	2.1	31.8	2.8	29.0	2.8	25.3	3.1
Crept blanket	168	0	44.8	0.2	43.5	0.2	40.6	0.5	38.4	0.9	35.7	0.9	33.7	1.5	31.2	1.0

APPENDIX 11: Aged plasticity of various samples subjected isothermal heating at 140°C at different ageing-periods.

			Wallace plasticity, (1/100)mm at 140 heat-							g time	e:					
Pre-treatment	Maturation		0 mi	0 min		n	10 m	in	15 m	in	20 m	in	25 m	in	30 m	in
type	period h	[H3PO4] %	Mean	S P	Mean	S P	Mean	S P	Mean	s e	Mean	S P	Mean	s e	Mean	s e
Agglomerated	<u>168</u>	1	35.3	43	30.9	47	26.2	<u>3.c</u>	21.8	<u> </u>	17.3	3.0	12.3	2.5	9.6	$\frac{3.0}{2.4}$
Free cuplumps	168	1	<i>41 4</i>	$\frac{1.5}{2.5}$	36.4	21	20.2	1.1	21.0	1.5	17.5	0.5	12.3	0.4	2.0 8.7	0.6
Slab cut	168	1	37.6	2.3	30.4	2.1 2.5	27.5	23	20.8	21	17.5	1.6	11.3	1.2	8.2	1.2
Macaratad	168	1	15 2	0.8	12.1	0.4	40.0	2.3	20.0	$^{2.1}$	36.4	0.3	33.2	0.0	31.6	0.8
Crept blanket	108	1	45.2	1.6	42.4	1.3	40.0	1.2	лз л	1.0	30.4 12.7	0.5	39.6	0.9	30.0	0.0
A galamaratad	100	1	43.0	2.0	24.0	2.4	20.2	2.2	12.4	2.2	10.6	1.1	12.0	1.0	39.0	1.0
Aggiomerated	108	2	39.0	5.0	25.0	J.4	29.2	0.0	23.0	3.3 0.5	19.0	1.4	12.0	1.9	9.5	1.9
Free cuplumps	108	2	39.5	1.2	35.2	1.4	29.1	0.8	22.0	0.5	10.7	0.7	10.7	1.1	8.0	0.5
Slab cut	168	2	36.3	2.9	31.8	3.3	21.2	3.2	21.0	3.0	15.3	1.9	10.8	1.5	7.8	1.5
Macerated	168	2	45.9	0.5	43.9	0.6	41.0	0.9	39.9	1.3	36.8	1.1	34.3	1.6	31.9	1.6
Crept blanket	168	2	48.8	1.9	48.2	2.0	46.8	1.7	44.8	1.0	42.2	0.6	40.8	0.5	39.7	0.7
Agglomerated	336	0	34.5	5.9	29.9	5.9	24.5	4.9	17.1	4.1	16.2	3.5	10.7	2.6	7.5	1.7
Free cuplumps	336	0	37.4	3.1	33.3	3.4	26.4	2.7	21.0	2.0	15.5	1.0	11.4	0.8	8.3	0.6
Slab cut	336	0	37.4	4.2	32.1	4.5	< 27.1	4.2	21.1	3.7	16.5	2.8	11.6	2.3	8.1	1.5
Macerated	336	0	49.0	0.8	45.5	0.3	44.2	0.1	41.3	0.5	38.2	0.1	35.6	0.4	33.3	0.3
Crept blanket	336	0	51.8	0.4	48.8	0.8	46.7	0.6	44.5	1.1	42.1	0.6	40.3	1.0	39.3	0.7
Agglomerated	336	1	36.1	6.3	27.4	5.1	22.8	4.8	22.4	4.9	19.4	4.2	14.8	3.7	11.4	3.0
Free cuplumps	336	1	40.9	2.1	36.6	2.1	34.2	3.0	25.7	1.4	21.5	1.3	14.8	0.6	10.5	0.8
Slab cut	336	1	42.5	3.2	36.5	2.8	32.4	2.9	26.1	2.8	21.7	2.4	16.1	2.1	11.2	1.9
Macerated	336	1	50.9	0.9	46.7	0.4	44.7	0.2	42.1	0.3	39.5	0.2	37.2	0.4	34.3	0.3
Crept blanket	336	1	53.5	1.3	50.9	0.4	49.5	0.6	48.3	0.5	47.0	0.5	43.7	0.5	42.2	0.5

**APPENDIX 11:** Aged plasticity of various samples subjected isothermal heating at 140°C at different ageing-periods (continued)

			Wallac	e pals	sticity, (1	/100)	mm at 140 heat-ageing time:									
Dra traatmant	Maturation		0 m	in	5 mi	n	10 m	in	15 m	nin	20 m	in	25 m	nin	30 m	nin
type	period h	[ <b>H3PO</b> /1] %	Mean	6 8	Mean	C A	Mean	C A	Mean	C A	Mean	6 0	Mean	6 0	Mean	6 0
Agglomorated	226	2	27.2	6.0	22.9	6.2	29.5	5.0	22.5	5.0	20.2	1.0	15 /	3.C	11 7	2.4
Aggiomerated	550	2	37.3	0.0	20.7	0.5	20.5	3.3	25.5	3.3	20.5	4.0	15.4	4.1	11./	5.4
Free cuplumps	336	2	40.8	2.0	36.7	2.6	31.2	2.1	26.2	2.1	21.2	1.6	15.3	1.2	11.1	0.9
Slab cut	336	2	40.8	3.0	34.9	3.3	31.7	3.4	25.9	3.1	20.8	2.8	15.7	2.4	11.0	2.2
Macerated	336	2	50.8	1.1	47.7	0.8	45.7	0.7	43.7	0.7	41.2	0.8	38.7	0.5	35.9	0.4
Crept blanket	336	2	53.5	1.5	50.4	0.4	48.2	0.3	47.6	0.2	46.8	0.5	44.1	0.6	41.7	0.3
Agglomerated	504	0	35.7	2.8	31.4	3.0	26.8	2.3	21.4	1.9	17.9	1.2	14.3	0.9	11.3	1.5
Free cuplumps	504	0	41.3	1.9	36.6	1.6	33.4	1.6	28.3	0.8	23.7	0.2	18.8	0.4	15.3	0.5
Slab cut	504	0	41.7	2.3	38.3	2.5	33.9	2.6	29.4	2.0	25.3	2.2	19.6	1.8	15.0	1.6
Macerated	504	0	51.0	0.8	47.8	0.9	45.7	1.1	43.3	1.0	41.7	1.2	39.2	1.2	36.8	1.3
Crept blanket	504	0	52.8	0.7	49.9	0.7	48.0	0.7	45.4	0.7	44.6	0.8	42.7	0.8	41.7	1.0
Agglomerated	504	1	39.8	1.5	35.3	2.2	31.2	1.6	26.8	1.8	22.3	2.1	16.8	1.1	14.2	1.9
Free cuplumps	504	1	44.1	1.2	41.1	1.5	35.7	0.7	31.4	0.5	27.0	0.5	21.0	0.7	17.1	0.9
Slab cut	504	1	47.0	2.2	42.7	2.1	38.2	2.1	34.1	1.7	28.7	1.8	22.8	1.1	18.1	1.0
Macerated	504	1	51.9	0.9	49.4	0.6	48.0	0.8	45.2	1.0	45.7	2.4	41.4	1.4	39.8	1.5
Crept blanket	504	1	54.6	0.4	52.1	0.6	50.9	0.4	48.5	0.5	47.2	0.3	44.9	0.5	43.8	0.4
Agglomerated	504	2	41.8	2.2	37.7	2.3	33.9	2.4	28.9	2.6	24.3	2.2	19.5	1.9	16.4	2.4
Free cuplumps	504	2	45.3	0.9	41.3	0.8	36.9	0.4	32.3	0.3	28.8	0.3	22.8	1.1	19.5	1.0
Slab cut	504	2	43.8	0.7	40.3	1.0	36.6	1.2	31.4	0.8	26.8	0.7	22.0	0.8	18.9	1.3
Macerated	504	2	53.8	0.7	50.5	0.9	49.3	0.5	46.8	0.5	44.3	0.9	42.0	0.8	40.1	1.0
Crept blanket	504	2	54.8	0.2	52.1	0.6	48.8	0.6	47.1	0.5	46.7	0.6	45.3	0.4	43.7	0.8

**APPENDIX 11:** Aged plasticity of various samples subjected isothermal heating at 140°C at different ageing-periods (continued)

			Wallac	e pals	sticity, (I	l/100,	)mm at I	40 he	eat-agein	g tim	e:					
Pre-treatment	Maturation		0 m	in	5 m	in	$-10 \mathrm{m}$	1111115 min		in	$n = 20 \min$		25 min		30 m	in
type	neriod h	[H3PO4] %	Mean	S P	Mean	SP	Mean	s e	Mean	se	Mean	s e	Mean	se	Mean	se
Agglomerated	<u>672</u>	0	36.8	<u> </u>	31.1	4 1	28.2	4.3	23.8	<u> </u>	20.8	3.8	15.8	3.3	11.0	$\frac{3.0}{2.4}$
Free cuplumps	672	0	37.5	3.6	33.1	33	28.0	27	21.6	17	17.1	1.1	12.5	0.5	9.8	0.7
Slab cut	672	0	40.2	2.0	35.0	2.8	20.0	$\frac{2.7}{2.1}$	21.0 25.2	1.7	10.1	1.1 1.2	12.5	0.5	10.0	1.2
Macoratad	672	0	+0.2 52.8	2.0	10.8	0.4	177	2.4	15 3	0.4	12.1	1.2	12.7	0.5	27.8	0.0
Cront blonket	672	0	51 0	0.0	49.0	1.0	47.7	0.2	45.5	0.4	43.3	1.2	40.3	0.0	20.8	0.9
Crept blanket	072	0	31.8	0.7	49.3	1.0	48.0	1.1	43.8	1.1	43.7	1.2	41.8	1.2	39.8	0.9
Agglomerated	672	1	39.3	4.6	37.0	5.4	32.8	4.5	28.3	4.7	24.3	4.4	19.4	4.0	14.1	3.2
Free cuplumps	672	1	38.4	2.6	34.4	2.5	29.5	1.9	25.5	1.5	20.0	0.8	15.2	0.6	10.9	0.2
Slab cut	672	1	40.3	1.5	36.2	1.7	32.3	2.0	27.3	1.1	22.4	1.0	17.3	0.5	12.8	0.7
Macerated	672	1	51.8	0.9	47.9	0.3	45.9	0.3	44.2	0.2	41.3	0.6	39.8	0.3	37.3	0.4
Crept blanket	672	1	53.9	0.4	51.5	0.5	48.8	0.6	45.5	0.4	44.5	0.7	42.8	0.6	40.8	0.9
Agglomerated	672	2	41.6	4.1	37.9	4.2	33.7	4.0	29.9	3.9	24.8	3.3	20.8	3.1	14.0	1.9
free cuplumps	672	2	37.9	2.2	34.3	2.4	28.9	1.5	24.8	1.1	18.8	0.3	15.5	0.3	11.2	0.5
Slab cut	672	2	<b>3</b> 9.7	1.2	37.0	1.5	32.3	1.2	27.2	0.5	22.3	0.2	17.0	0.6	12.8	0.7
Macerated	672	2	51.2	0.6	48.6	0.7	47.1	0.7	44.7	0.9	43.4	0.8	40.5	0.9	38.4	1.2
Crept blanket	672	2	50.1	1.0	48.3	1.5	46.8	1.5	43.7	1.6	43.4	1.6	41.7	1.7	39.4	1.8
				< m	25.44	- 53										

APPENDIX 11: Aged plasticity of various samples subjected isothermal heating at 140°C at different ageing-periods (continued).

			In (Po), at 140 heat-ageing with a time of :								
<b>Pre-treatment</b>	Maturation	[H3PO4],									
type	period, h	%	0 min	5 min	10 min 🧹	15 min	20 min	25 min	30 min		
Agglomerated	0	0	3.8	3.7	3.7	3.6	3.4	3.3	3.1		
free cuplumps	0	0	3.8	3.7	3.7	3.6	3.4	3.3	3.1		
slab cut	0	0	3.8	3.7	3.7	3.6	3.4	3.3	3.1		
macerated	0	0	3.8	3.7	3.7	3.6	3.4	3.3	3.1		
crept blanket	0	0	3.8	3.7	3.7	3.6	3.4	3.3	3.1		
Agglomerated	0	1	3.8	3.7	3.7	3.6	3.4	3.3	3.1		
free cuplumps	0	1	3.8	3.7	3.7	3.6	3.4	3.3	3.1		
slab cut	0	1	3.8	3.7	3.7	3.6	3.4	3.3	3.1		
macerated	0	1	3.8	3.7	3.7	3.6	3.4	3.3	3.1		
crept blanket	0	1	3.8	3.7	3.7	3.6	3.4	3.3	3.1		
Agglomerated	0	2	3.8	3.7	3.7	3.6	3.5	3.4	3.2		
free cuplumps	0	2	3.8	3.7	3.7	3.6	3.5	3.4	3.2		
slab cut	0	2	3.8	3.7	3.7	3.6	3.5	3.4	3.2		
macerated	0	2	3.8	3.7	3.7	3.6	3.5	3.4	3.2		
crept blanket	0	2	3.8	3.7	3.7	3.6	3.5	3.4	3.2		
Agglomerated	168	0	3.5	3.4	3.1	2.8	2.5	2.2	1.8		
free cuplumps	168	0	3.5	3.4	3.1	2.8	2.5	2.1	1.7		
slab cut	168	0	3.5	3.3	3.1	2.8	2.4	2.0	1.6		
macerated	168	0	3.8	3.7	3.7	3.6	3.5	3.4	3.2		
crept blanket	168	0	3.8	3.8	3.7	3.6	3.6	3.5	3.4		

#### **APPENDIX 12(a):** Natural logarithm of aged plasticity of the various samples subjected isothermal heating

at 140°C at different ageing-periods.

							107				
			In (Po), at 140 heat-ageing with a time of :								
Pre-treatment	Maturation	[H3PO4],	IXI VOUI								
type	period,h	%	0 min	5 min	10 min	15 min	20 min	25 min	30 min		
Agglomerated	168	1	3.6	3.4	3.3	3.1	2.8	2.5	2.3		
free cuplumps	168	1	3.7	3.6	3.4	3.1	2.9	2.5	2.2		
slab cut	168	1	3.6	3.5	3.3	3.0	2.8	2.4	2.1		
macerated	168	1	3.8	3.7	3.7	3.6	3.6	3.5	3.5		
crept blanket	168	1	3.8	3.8	3.8	3.8	3.8	3.7	3.7		
Agglomerated	168	2	3.7	3.6	3.4	3.2	3.0	2.5	2.3		
free cuplumps	168	2	3.7	3.6	3.4	3.1	2.8	2.4	2.1		
slab cut	168	2	3.6	3.5	3.3	3.0	2.7	2.4	2.0		
macerated	168	2	3.8	3.8	3.7	3.7	3.6	3.5	3.5		
crept blanket	168	2	3.9	3.9	3.8	3.8	3.7	3.7	3.7		
Agglomerated	336	0	3.5	3.4	3.2	2.8	2.8	2.4	2.0		
free cuplumps	336	0	3.6	3.5	3.3	3.0	2.7	2.4	2.1		
slab cut	336	0	3.6	3.5	3.3	3.0	2.8	2.5	2.1		
macerated	336	0	3.9	3.8	3.8	3.7	3.6	3.6	3.5		
crept blanket	336	0	3.9	3.9	3.8	3.8	3.7	3.7	3.7		
Agglomerated	336	1	3.6	3.3	3.1	3.1	3.0	2.7	2.4		
free cuplumps	336	1	3.7	3.6	3.5	3.2	3.1	2.7	2.4		
slab cut	336	1	3.7	3.6	3.5	3.3	3.1	2.8	2.4		
macerated	336	1	3.9	3.8	3.8	3.7	3.7	3.6	3.5		
crept blanket	336	1	4.0	3.9	3.9	3.9	3.9	3.8	3.7		

**APPENDIX 12(a):** Natural logarithm of aged plasticity of the various samples subjected isothermal heating

at 140°C at different ageing-periods (continued).

		IZNILICT									
<b>Pre-treatment</b>	Maturation			ln (F	<b>Po)</b> , at 140	heat-agei	ng with a t	time of :			
type	period,h	[H3PO4],%	0 min	5 min	10 min	15 min	20 min	25 min	30 min		
Agglomerated	336	2	3.6	3.5	3.3	3.2	3.0	2.7	2.5		
free cuplumps	336	2	3.7	3.6	3.4	3.3	3.1	2.7	2.4		
slab cut	336	2	3.7	3.6	3.5	3.3	3.0	2.8	2.4		
macerated	336	2	3.9	3.9	3.8	3.8	3.7	3.7	3.6		
crept blanket	336	2	4.0	3.9	3.9	3.9	3.8	3.8	3.7		
Agglomerated	504	0	3.6	3.4	3.3	3.1	2.9	2.7	2.4		
free cuplumps	504	0	3.7	3.6	3.5	3.3	3.2	2.9	2.7		
slab cut	504	0	3.7	3.6	3.5	3.4	3.2	3.0	2.7		
macerated	504	0	3.9	3.9	3.8	3.8	3.7	3.7	3.6		
crept blanket	504	0	4.0	3.9	3.9	3.8	3.8	3.8	3.7		
Agglomerated	504	1	3.7	3.6	3.4	3.3	3.1	2.8	2.7		
free cuplumps	504	1	3.8	3.7	3.6	3.4	3.3	3.0	2.8		
slab cut	504	1	3.9	3.8	3.6	3.5	3.4	3.1	2.9		
macerated	504	1	3.9	3.9	3.9	3.8	3.8	3.7	3.7		
crept blanket	504	1	4.0	4.0	3.9	3.9	3.9	3.8	3.8		
Agglomerated	504	2	3.7	3.6	3.5	3.4	3.2	3.0	2.8		
free cuplumps	504	2	3.8	3.7	3.6	3.5	3.4	3.1	3.0		
slab cut	504	2	3.8	3.7	3.6	3.4	3.3	3.1	2.9		
macerated	504	2	4.0	3.9	3.9	3.8	3.8	3.7	3.7		
crept blanket	504	2	4.0	4.0	3.9	3.9	3.8	3.8	3.8		

**APPENDIX 12(a):** Natural logarithm of aged plasticity of the various samples subjected isothermal heating

at 140°C at different ageing-periods (continued).

							ICT				
			In (Po), at 140 heat-ageing with a time of :								
<b>Pre-treatment</b>	Maturation	[H3PO4],									
type	period, h	%	0 min	5 min	10 min	15 min	20 min	25 min	30 min		
Agglomerated	672	0	3.6	3.4	3.3	3.2	3.0	2.8	2.4		
free cuplumps	672	0	3.6	3.5	3.3	3.1	2.8	2.5	2.3		
slab cut	672	0	3.7	3.6	3.4	3.2	2.9	2.6	2.4		
macerated	672	0	4.0	3.9	3.9	3.8	3.8	3.7	3.6		
crept blanket	672	0	3.9	3.9	3.9	3.8	3.8	3.7	3.7		
Agglomerated	672	1	3.7	3.6	3.5	3.3	3.2	3.0	2.6		
free cuplumps	672	1	3.6	3.5	3.4	3.2	3.0	2.7	2.4		
slab cut	672	1	3.7	3.6	3.5	3.3	3.1	2.9	2.6		
macerated	672	1	3.9	3.9	3.8	3.8	3.7	3.7	3.6		
crept blanket	672	1	4.0	3.9	3.9	3.8	3.8	3.8	3.7		
Agglomerated	672	2	3.7	3.6	3.5	3.4	3.2	3.0	2.6		
free cuplumps	672	2	3.6	3.5	3.4	3.2	2.9	2.7	2.4		
slab cut	672	2	3.7	3.6	3.5	3.3	3.1	2.8	2.6		
macerated	672	2	3.9	3.9	3.9	3.8	3.8	3.7	3.6		
Crept blanket	672	2	3.9	3.9	3.8	3.8	3.8	3.7	3.7		

**APPENDIX 12(a):** Natural logarithm of aged plasticity of the various samples subjected isothermal heating

at 140°C at different ageing-periods (continued).





Figure AP12-1 Plot of ln(P) versus ageing time for cuplumps

Figure AP12-2 Plot of ln(P) versus ageing time for cuplumps

processed at 0 h maturation and 1% phosphoric acid

processed after 168 h of maturation and 1% phosphoric acid treatment.

crumb treatment.





Figure AP12-3 Plot of ln(P) versus ageing time for cuplumps

Figure AP12-4 Plot of ln(P) versus ageing time for cuplumps

processed at 336 h maturation and 1% phosphoric acid

processed after 504 h of maturation and 1% phosphoric acid

crumb treatment.

crumb treatment.



processed at 672 h maturation and 1% phosphoric acid

crumb treatment.

SANE N





crumb treatment.

crumb treatment.



Figure AP12-10 Plot of ln(P) versus ageing time for cuplumps

processed at 672 h maturation and 2% phosphoric acid

crumb treatment.

#### **APPENDIX 13: Degradation constants of pre-treated cuplumps under varying**

#### maturation periods.

Rubber	Phosphoric	Degradat	ion constant	t k, min <sup>-1</sup> (at	a maturatio	n period )
Sample	Acid	0 h	168 h	336 h	504 h	672 h
	0%	-0.0240	-0.0577	-0.0503	-0.0387	-0.0377
Agglomerated	1%	-0.0222	-0.0441	-0.0346	-0.0351	-0.0334
	2%	-0.0188	-0.0478	-0.0386	-0.0318	-0.0341
Erroo	0%	-0.0240	-0.0163	-0.0515	-0.0332	-0.0463
Free	1%	-0.0222	-0.0528	-0.0454	-0.0319	-0.0414
cuplumps	2%	-0.0188	-0.0552	-0.0432	-0.0283	-0.0406
	0%	-0.0240	-0.0654	-0.0509	-0.0336	-0.0460
Slab- cut	1%	-0.0222	-0.0512	-0.0432	-0.0315	-0.0376
	2%	- <mark>0.0188</mark>	-0.0526	-0.0425	-0.0289	-0.0380
	0%	-0.0240	-0.0183	-0.0129	-0.0105	-0.0108
Macerated	1%	-0.0222	-0.0118	-0.0126	-0.0086	-0.0105
	2%	-0.0188	-0.0121	-0.0111	-0.0097	-0.0093
Creat	0%	-0.0240	-0.0124	-0.0093	-0.0079	-0.0083
Crept blankets	1%	-0.0222	-0.0052	-0.0076	-0.0074	-0.0093
	2%	-0.0188	-0.0076	-0.0075	-0.0072	-0.0078

Source: Experimental data, 2011.



			Walla	ace Plast	icity,	(1/100)r	nm pe	r matura	tion p	eriod	
	[H3PO4],	0 h	l	168	168 h		336 h		504 h		h
Pre-treatment	%	mean	s.e	mean	s.e	mean	s.e	mean	s.e	mean	s.e
	0	44.7	0.5	33.5	3.2	34.5	5.9	35.7	2.8	36.8	4.9
	1	44.8	1.0	35.3	4.3	36.1	6.3	39.8	1.5	39.3	4.6
Agglomerated	2	44.2	0.5	39.6	3.0	37.3	6.0	41.8	2.2	41.6	4.1
	0	44.7	0.5	33.5	1.2	37.4	3.1	41.3	1.9	37.5	3.6
	1	44.8	1.0	41.4	2.5	40.9	2.1	44.1	1.2	38.4	2.6
Free cuplumps	2	44.2	0.5	39.5	1.2	40.8	2.0	45.3	0.9	37.9	2.2
	0	44.7	0.5	32.6	1.0	37.4	4.2	41.7	2.3	40.2	2.8
	1	44.8	1.0	37.6	2.2	42.5	3.2	47.0	2.2	40.3	1.5
Slab cut	2	44.2	0.5	36.3	2.9	40.8	3.0	43.8	0.7	39.7	1.2
	0	44.7	0.5	4 <mark>3.8</mark>	1.6	<b>4</b> 9.0	0.8	51.0	0.8	52.8	0.6
	1	44.8	1.0	45.2	0.8	50.9	0.9	51.9	0.9	51.8	0.9
Macerated	2	44.2	0.5	45.9	0.5	50.8	1.1	53.8	0.7	51.2	0.6
	0	44.7	0.5	44.8	0.2	51.8	0.4	52.8	0.7	51.8	0.7
	1	44.8	1.0	45.8	1.6	53.5	1.3	54.6	0.4	53.9	0.4
Crept blanket	2	44.2	0.5	48.8	1.9	53.5	1.5	54.8	0.2	50.1	1.0

APPENDIX 14: Wallace plasticity of samples obtained under the mechanical pre-treatment at maturation periods of 0h -

IZE IL IOT

672h.

#### **APPENDIX 15:** The % non-rubber fraction extracted from each mechanical pre-treated sample.

Sample	Non-isoprene constituents lost	PRI, % (at a maturation period of)							
bumple	treatment equipment, % weight	0 h	168 h	336 h	504 h	672 h			
Agglomerated	-	52.0 ± 1.5	<u>19.5+</u> 2.3	24.2±0.5	29.8 <u>+</u> 0.5	34.4 <u>+</u> 0.9			
Free cuplumps		52.0 ± 1.5	14.5 <u>+</u> 1.7	21.6±0.2	32.2 <u>+</u> 0.9	24.2 <u>+</u> 1.0			
Slab-cut	4.7%±1.5%	52.0 ± 1.5	15.7 <u>±</u> 0.3	24.5±0.4	39.4 <u>+</u> 1.2	29.0±1.5			
Macerated	8.4%±1.3%	52.0 <u>+</u> 1.5	44.4 <u>+</u> 1.3	65.3 <u>±</u> 0.8	69.4 <u>+</u> 0.7	67.6 <u>+</u> 3.3			
Crept blankets	15.9%±0.4%	52.0 ± 1.5	64.4 <u>±</u> 0.1	73.5 <u>+</u> 2.3	76.5 <u>+</u> 3.3	74.5 <u>+</u> 2.0			

Source: Experimental computation, 2011.

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<b>APPENDIX 16:</b>	Effect of	of phosphoric	acid	treatment of	on PRI	of	crumbs	obtained	through	different	pre-treatmen	t and
maturation.												

KNIIST											
				PR	<b>RI, %</b> ]	per mati	uratio	n period	1		
		0 h	ı	168	168 h		336 h		504 h		h
pre-treatment	[H3PO4],%	mean	s.e	mean	s.e	mean	s.e	mean	s.e	mean	s.e
	0	48.6	1.7	17.6	1.0	20.5	1.5	32.3	5.1	28.1	2.8
	1	50.9	1.6	24.8	3.9	28.7	3.4	35.0	3.3	33.4	4.2
Agglomerated	2	56.5	1.9	22.9	3.0	27.4	4.8	38.3	3.8	33.1	1.3
	0	48.6	1.7	16.3	1.0	22.1	0.2	37.7	2.8	26.3	0.7
	1	50.9	1.6	20.9	0.5	25.5	0.7	39.2	3.2	29.0	1.9
free cuplumps	2	56.5	1.9	20.5	1.7	27.0	0.8	43.4	3.2	30.3	3.0
	0	48.6	1.7	14.5	0.6	20.6	1.8	35.5	1.8	26.8	1.2
	1	50.9	1.6	21.2	2.0	25.4	2.9	38.4	0.4	31.8	1.0
slab cut	2	56.5	1.9	20.4	2.4	25.7	3.6	43.1	2.3	32.7	2.6
	0 🥪	48.6	1.7	56.9	5.1	67.9	1.2	72.1	1.6	71.7	1.9
	1	50.9	1.6	70.2	2.8	67.5	1.2	76.6	2.6	72.1	1.7
macerated	2	56.5	1.9	69.4	3.0	70.9	1.4	74.4	1.2	75.0	1.7
	0	48.6	1.7	69.5	2.3	76.0	1.6	78.8	1.3	76.7	1.1
	1	50.9	1.6	85.5	2.3	79.1	2.5	80.3	1.0	75.6	1.4
crept blanket	2	56.5	1.9	81.6	1.8	78.3	2.7	79.6	1.2	78.5	2.2

		Colour			
Maturation	Pre-treatment	Mean	s.d	s.e	
	agglomerated	5	0.5	0.25	
	free cuplumps	5	0.5	0.25	
Oh	Slab-cut	5	0.5	0.25	
	macerated	5	0.5	0.25	
	crept blankets	5	0.5	0.25	
	agglomerated	7	0.8	0.41	- T
	free cuplumps	6	0.5	0.25	
168h	Slab-cut	8	0.5	0.25	
	macerated	8	0.5	0.25	
	crept blankets	10	0.5	0.25	
	agglomerated	6	0.5	0.25	
	free cuplumps	7	0.5	0.25	
336h	Slab- cut	8	0.8	0.41	
	macerated	9	0.5	0.25	
	crept blankets	11	1.0	0.50	
	agglomerated	7	0.5	0.25	
	free cuplumps	7	0.5	0.25	
504h	Slab-cut	8	0.5	0.25	
	macerated	11	0.6	0.29	
	crept blankets	12	0.5	0.25	
	agglomerated	7	1.0	0.48	
	free cuplumps	8	0.0	0.00	
672h	Slab-cut	8	0.5	0.25	
	macerated	11	1.2	0.58	
	crept blankets	14	1.0	0.50	

#### **APPENDIX 17: Colour (Lovibond) of dried NR obtained from different pre**treatment and maturation periods

		(ML, 1+4, 1	.00)
	Pre-treatment		
Aaturation	Sample	Mean	s.e
	agglomerated	86.1	1.9
	free cuplumps	86.1	1.9
0h	slab-cut	86.1	1.9
	macerated	86.1	1.9
	crept blankets	86.1	1.9
	agglomerated	78.1	6.0
	free cuplumps	72.0	4.7
168h	slab-cut	76.6	4.2
	macerated	82.6	1.0
	crept blankets	79.6	2.3
	agglomerated	77.0	5.2
	free cuplumps	78.3	3.2
336h	slab-cut	84.5	4.3
	macerated	88.4	2.8
	crept blankets	84.8	2.4
	agglomerated	77.6	5.5
	free cuplumps	79.6	5.0
504h	slab-cut	82.7	4.4
	macerated	88.1	1.9
	crept blankets	88.7	2.0
	agglomerated	88.7	4.7
	free cuplumps	89.2	3.0
672h	slab-cut	90.7	3.0
	macerated	89.3	1.9
	crept blankets	89.3	1.7

#### **APPENDIX 18:** Mooney viscosities of each sample after processing

		[H <sub>2</sub> PO <sub>4</sub> ] before		Abs	sorbance rea			
Maturation	pre-treatment	treatment, %	1st	2nd	3rd	Mean	s.d	[H <sub>3</sub> PO <sub>4</sub> ] after treatment, %
Oh	All	1.1	0.600	0.578	0.602	0.593	0.013	1.0
	Agglomerated	1.1	0.563	0.576	0.569	0.569	0.007	1.0
	free cuplumps	1.1	0.574	0.574	0.574	0.574	0.000	1.0
	jumbo slabbed	1.1	0.578	0.578	0.577	0.578	0.001	1.0
	macerated	1.1	0.584	0.584	0.583	0.584	0.001	1.0
168h	crept blankets	1.1	0.581	0.582	0.581	0.581	0.001	1.0
	Agglomerated	1.1	0.571	0.584	0.577	0.577	0.007	1.0
	free cuplumps	1.1	0.582	0.583	0.582	0.582	0.001	1.0
	jumbo slabbed	1.1	0.596	0.595	0.595	0.595	0.001	1.1
	macerated	1.1	0.579	0.579	0.579	0.579	0.000	1.0
336h	crept blankets	1.1	0.591	0.592	0.591	0.591	0.001	1.0
	Agglomerated	1.1	0.564	0.594	0.577	0.578	0.015	1.0
	free cuplumps	1.1	0.597	0.595	0.596	0.596	0.001	1.1
	jumbo slabbed	1.1	0.591	0.590	0.590	0.590	0.001	1.0
	macerated	1.1	0.616	0.618	0.617	0.617	0.001	1.1
504h	crept blankets	1.1	0.599	0.598	0.598	0.598	0.001	1.1
	Agglomerated	1.1	0.607	0.619	0.613	0.613	0.006	1.1
	free cuplumps	1.1	0.591	0.59	0.591	0.591	0.001	1.0
	jumbo slabbed	1.1	0.607	0.606	0.605	0.606	0.001	1.1
	macerated	1.1	0.590	0.590	0.591	0.590	0.001	1.0
672h	crept blankets	1.1	0.604	0.603	0.605	0.604	0.001	1.1

<b>APPENDIX 19(a): Exp</b>	erimental data on 1%	phosphoric acid inta	ake by crumbs	(Experimental data	, 2011).
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		[H <sub>3</sub> PO <sub>4</sub> ] before		Absorba	ance readings			[H <sub>3</sub> PO <sub>4</sub> ] after
Maturation	pre-treatment	treatment, %	1st reading	2nd reading	3rd reading	average	s.d	treatment, %
Oh	All	2.2	1.190	1.187	1.198	1.192	0.006	2.1
	Agglomerated	2.2	1.100	1.133	1.135	1.123	0.020	2.0
	Free cuplumps	2.2	1.153	1.155	1.154	1.154	0.001	2.0
	Jumbo slabbed	2.2	1.141	1.143	1.142	1.142	0.001	2.0
	Macerated	2.2	1.157	1.165	1.159	1.160	0.004	2.0
168h	Crept blankets	2.2	1.176	1.183	1.180	1.180	0.004	2.1
	Agglomerated	2.2	1.189	1.106	1.106	1.134	0.048	2.0
	Free cuplumps	2.2	1.154	1.153	1.153	1.153	0.001	2.0
	Jumbo slabbed	2.2	1.169	1.168	1.168	1.168	0.001	2.1
	Macerated	2.2	1.200	1.200	1.280	1.227	0.046	2.2
336h	Crept blankets	2.2	1.183	1.186	1.184	1.184	0.002	2.1
	Agglomerated	2.2	1.192	1.194	1.195	1.194	0.002	2.1
	Free cuplumps	2.2	1.177	1.175	1.176	1.176	0.001	2.1
	Jumbo slabbed	2.2	1.145	1.147	1.146	1.146	0.001	2.0
	Macerated	2.2	1.202	1.204	1.203	1.203	0.001	2.1
504h	Crept blankets	2.2	1.256	1.258	1.255	1.256	0.002	2.2
	Agglomerated	2.2	1.151	1.165	1.151	1.156	0.008	2.0
	Free cuplumps	2.2	1.235	1.236	1.235	1.235	0.001	2.2
	Jumbo slabbed	2.2	1.185	1.184	1.180	1.183	0.003	2.1
	Macerated	2.2	1.228	1.229	1.228	1.228	0.001	2.2
672h	Crept blankets	2.2	1.238	1.239	1.238	1.238	0.001	2.2

APPENDIX 19(b): Experimental data on 2% phosphoric acid intake by crumbs (Experimental data, 2011).

### **APPENDIX 19(c): Sample calculations for % phosphoric acid in solution determination by spectrometry.**

e.g. Absorbance reading for blank solution used during 1% and 2% phosphoric acid solutions tests were:

for 1% = 0.000, 0.004, 0.002, 0.001; and for 2% = 0.001, 0.000, 0.004, 0.000.

therefore, average absorbance reading for 1% blank was

$$\frac{0.000 + 0.004 + 0.002 + 0.001}{4} = 0.00175$$
$$\therefore [H_3PO_4] = k \times 0.00175$$
$$where \ k = \frac{1}{M};$$

and M = slope of the calibration curve



Figure AP19 Calibration curve for the determination of % phosphoric acid concentration of a solution by spectrometry.

*hence*,  $[H_3PO_4] = 1.764 \times 0.00175$ 

 $= 0.003\% \approx 0.0\%$  (when rounded to one decimal place)

		Α	В	С	D	E	F	G	Η	Ι	J	K	L	Μ	Ν	0	Р	Q	R	S	Т	U	V	W	Χ	Y
0h	FRESH	4	3	4	4	4	4	3	2	4	4	5	4	5	4	4	4	3	3	4	4	4	4	4	4	3
	AGGLOMERATED	4	5	4	5	4	4	4	5	4	5	4	4	4	4	5	4	4	4	2	4	4	4	3	4	5
	FREE CUPLUMPS	4	4	4	4	4	4	4	3	4	5	4	4	4	4	4	4	4	4	3	4	4	4	3	4	4
	SLAB-CUT	3	4	4	3	3	4	4	4	2	4	4	4	5	4	3	3	3	4	4	4	5	4	4	3	4
	MACERATED	3	3	4	4	4	3	4	4	4	3	3	1	3	4	4	4	4	3	3	3	4	4	4	3	3
168h	CREPT BLANKETS	3	3	3	4	3	4	3	3	2	3	2	3	2	3	3	3	2	3	3	3	2	3	3	3	2
	AGGLOMERATED	4	4	5	4	4	5	4	4	3	2	4	2	4	4	4	3	3	4	4	3	5	3	4	2	4
	FREE CUPLUMPS	4	3	4	3	4	3	4	3	2	3	3	3	3	2	5	4	4	5	4	3	3	3	3	3	3
	SLAB-CUT	3	3	4	3	4	4	4	4	3	3	3	3	2	4	3	3	3	4	3	4	4	4	3	4	3
	MACERATED	2	3	3	3	2	2	3	3	3	2	3	4	2	5	2	3	2	3	3	2	4	2	2	2	4
336h	CREPT BLANKETS	1	1	1	2	2	4	1	1	1	1	4	1	1	1	1	2	2	2	2	1	2	2	3	1	1
	AGGLOMERATED	5	4	5	4	4	4	5	4	4	3	1	4	5	5	5	3	4	5	3	3	4	4	4	3	5
	FREE CUPLUMPS	4	4	4	5	3	5	5	3	2	4	4	4	4	4	5	5	4	4	3	3	3	4	4	5	5
	SLAB-CUT	3	3	4	4	5	5	3	5	4	3	3	4	5	5	4	4	4	5	5	4	4	2	3	3	4
	MACERATED	2	2	2	1	2	2	2	2	3	5	2	2	2	1	2	2	3	2	2	2	3	3	3	2	2
504h	CREPT BLANKETS	0	0	1	1	1	1	1	0	3	0	1	0	0	0	1	0	1	0	1	1	1	1	1	1	1
	AGGLOMERATED	5	4	5	4	4	4	5	4	4	3	1	4	5	5	5	3	4	5	3	3	4	4	4	3	5
	FREE CUPLUMPS	3	4	4	3	3	4	4	4	2	4	4	4	5	4	5	5	3	4	4	4	5	4	4	3	4
	SLAB-CUT	3	3	4	2	3	4	4	3	5	2	4	3	4	4	4	2	2	3	4	2	1	5	4	3	4
	MACERATED	2	1	2	1	2	2	2	2	2	2	2	2	2	2	2	1	1	2	2	2	2	4	2	2	2
672h	CREPT BLANKETS	0	0	1	1	1	1	0	1	1	1	1	1	1	1	1	1	1	1	1	0	2	1	1	0	0

#### APPENDIX 20: Odour Evaluation data based on Perrin –Koster approach

		Ζ	A'	Β'	C'	D'	E'	F'	G'	H'	I'	J'	K'	L'	M'	N'	0'	<b>P</b> '	Q'	R'	S'	Τ'	U'	V'	W'	Χ'
0h	FRESH	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	3	4	4	3	4	4	4	4	4	4
	AGGLOMERATED	5	5	4	5	5	3	4	5	4	5	4	4	4	5	4	4	4	4	4	4	4	4	4	4	5
	FREE CUPLUMPS	4	3	4	5	4	3	4	4	4	5	4	4	4	4	4	4	4	4	4	4	4	4	4	4	5
	SLAB-CUT	4	3	4	4	3	4	5	4	5	4	4	4	5	4	3	4	5	4	3	4	4	5	5	4	5
	MACERATED	4	4	3	4	3	4	3	4	4	4	4	3	3	3	4	4	4	4	3	4	5	4	4	4	4
168h	CREPT BLANKETS	4	2	3	4	4	3	4	3	2	3	3	3	3	3	3	3	4	2	2	2	3	2	3	2	3
	AGGLOMERATED	4	5	4	4	4	5	5	4	5	4	5	4	4	4	5	4	4	4	4	4	4	3	4	4	4
	FREE CUPLUMPS	3	3	4	3	4	5	4	4	4	4	4	3	4	4	3	4	4	3	4	4	4	4	3	4	3
	SLAB-CUT	4	3	4	4	4	4	4	4	5	4	2	2	3	3	3	4	3	4	2	4	3	4	3	4	2
	MACERATED	3	5	1	2	4	4	4	2	2	2	3	3	1	2	2	2	3	2	4	2	3	3	2	2	2
336h	CREPT BLANKETS	2	3	3	3	3	1	3	3	3	3	3	2	2	1	2	2	3	3	2	2	2	1	1	2	3
	AGGLOMERATED	4	5	2	4	2	3	3	4	4	5	3	5	3	4	3	3	3	4	5	5	4	4	3	5	4
	FREE CUPLUMPS	4	5	4	3	4	5	4	4	4	4	3	2	4	4	4	5	5	3	4	2	4	5	5	4	4
	SLAB-CUT	4	3	4	3	4	5	3	4	4	4	4	4	4	4	3	5	5	5	5	3	5	4	5	5	2
	MACERATED	2	2	2	2	3	5	1	1	1	2	2	1	0	0	0	1	1	2	2	1	1	1	2	2	3
504h	CREPT BLANKETS	1	1	1	1	1	1	1	1	1	1	0	0	0	1	1	2	2	0	1	1	1	0	1	1	2
	AGGLOMERATED	4	5	2	4	2	3	3	4	4	5	3	5	3	4	3	3	3	4	5	5	4	4	3	5	4
	FREE CUPLUMPS	4	3	4	4	3	4	5	4	5	4	4	4	5	4	3	4	5	4	3	4	4	5	5	4	5
	SLAB-CUT	5	5	5	3	4	3	3	4	5	2	2	4	4	5	3	4	5	3	5	4	5	4	5	3	4
	MACERATED	1	1	1	2	2	1	1	3	3	2	1	2	2	2	2	2	1	1	1	2	3	1	2	2	3
672h	CREPT BLANKETS	2	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

APPENDIX 20: Odour Evaluation data based on Perrin –Koster approach (Continued).

#### **APPENDIX 21:** Flowchart for the past and the future of cuplumps grade pretreatment and wet lines.



Note:

1. Agglo/ Fresh - a mixture of agglomerated and free cuplumps

# APPENDIX 22: ANOVA of PRI for agglomerated, free cuplumps, Slab-cut samples during the maturation periods for 0% phosphoric acid treatments, using Microsoft Office Excel, 2007.

Anova: Single Factor at 168 h maturation period.

SUMMARY				
Groups	Count	Sum	Average	Variance
Agglomerated	6	105.395	17.566	6.437
free cuplumps	6	97.778	16.296	5.742
slab cut	6	86.947	14.491	2.094

ANOVA				СТ		
Source of		(   )				
Variation	SS	df	MS	F	P-value	F crit
Between Groups	28.649	2	14.325	3.011	0.080	3.682
Within Groups	71.364	15	4.758			
Total	100.013	17	In.			

Significance level =0.05

Anova: Single Factor at 336 h maturation period

SUMMARY	1	Tr 1	1	2	
Groups	Count	Sum	Average	Variance	
Agglomerated	6	122.88	20.48	13.78	
free cuplumps	6	132.61	22.10	0.30	
slab cut	6	123.66	20.61	19.03	
ANOVA	22		5	185	
Source of Variation	SS	df	MS	F	P-value
Between Groups	9.741	2	4.871	0.441	0.651

Between Groups	9.741	2	4.871	0.441	0.651	3.682
Within Groups	165.530	15	11.035			
Total	175.271	17				

F crit

Significance level =0.05

#### APPENDIX 22: ANOVA of PRI values for Agglomerated, Free cuplumps, Slabcut samples during the maturation periods for 0% phosphoric acid treatments, using Microsoft Office Excel 2007 (continued).

SUMMARY						
Groups	Count	Sum	Average	Variance		
Agglomerated	6	193.617	32.269	154.365		
Free cuplumps	6	226.402	37.734	47.245		
Slab cut	6	213.073	35.512	19.847	_	
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	90.616	2	45.308	0.614	0.554	3.682
Within Groups	1107.280	15	73.819			
Total	1197.896	17				
Anova: Single Factor	at 672 h of	maturation	n period			
Anova: Single Factor SUMMARY Groups	at 672 h of	maturation	n period	Variance		
Anova: Single Factor SUMMARY Groups Agglomerated	at 672 h of Count	maturation	n period <u>Average</u> 28.111	Variance 46.671		
Anova: Single Factor SUMMARY Groups Agglomerated free cuplumps	at 672 h of <u>Count</u> 6 6	maturation <u>Sum</u> 168.667 157.758	Average 28.111 26.293	Variance 46.671 3.132		
Anova: Single Factor SUMMARY Groups Agglomerated free cuplumps slab cut	• at 672 h of <u>Count</u> 6 6 6	maturation Sum 168.667 157.758 161.053	Average 28.111 26.293 26.842	Variance 46.671 3.132 8.080		
Anova: Single Factor SUMMARY Groups Agglomerated free cuplumps slab cut	at 672 h of Count 6 6 6	<sup>2</sup> maturation <u>Sum</u> 168.667 157.758 161.053	Average 28.111 26.293 26.842	Variance 46.671 3.132 8.080		
Anova: Single Factor SUMMARY Groups Agglomerated free cuplumps slab cut	• at 672 h of <u>Count</u> 6 6 6 6	maturation Sum 168.667 157.758 161.053	Average 28.111 26.293 26.842	Variance 46.671 3.132 8.080		
Anova: Single Factor SUMMARY Groups Agglomerated free cuplumps slab cut ANOVA Source of Variation	at 672 h of <u>Count</u> 6 6 6 6	maturation Sum 168.667 157.758 161.053	Average 28.111 26.293 26.842 MS	Variance 46.671 3.132 8.080	P-value	F crit
Anova: Single Factor SUMMARY Groups Agglomerated free cuplumps slab cut ANOVA Source of Variation Between Groups	at 672 h of <u>Count</u> 6 6 6 6 7 10.436	maturation Sum 168.667 157.758 161.053 df 2	Average 28.111 26.293 26.842 <u>MS</u> 5.218	Variance 46.671 3.132 8.080 F 0.270	P-value 0.767	<u><i>F crit</i></u> 3.682
Anova: Single Factor SUMMARY Groups Agglomerated free cuplumps slab cut ANOVA Source of Variation Between Groups Within Groups	at 672 h of <u>Count</u> 6 6 6 6 7 10.436 289.413	r maturation Sum 168.667 157.758 161.053 df 2 15	Average 28.111 26.293 26.842 MS 5.218 19.294	Variance 46.671 3.132 8.080 F 0.270	<u>P-value</u> 0.767	<i>F crit</i> 3.682

Anova: Single Factor at 504 h of maturation period

Significance level =0.05