

## *Effects of Added Ammonium Laurate Soap on Natural Rubber Latex*

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*Low quality natural rubber latex, matured with different levels of well known long chain fatty acid salt showed variations in properties. Mechanical stability time, foaming height and viscosity were significantly altered by the added ammonium laurate soap level. Potassium hydroxide number and conductivity showed existence of a similar effect apparently up to a certain level of the added soap. Soap levels above  $0.5 \times 10^{-4}$  moles per 100 g of latex enhance the mechanical stability time as well as foaming height. Magnitude of the effect depends upon the amount of the added soap. Initial viscosity was decreased by soap addition but a progressive increase and corresponding decrease was observed thereafter. Both potassium hydroxide number and conductivity increased with increasing levels of soap and attained a constant value after  $5 \times 10^{-4}$  moles of soap per 100 g latex. Soap levels between  $4.2 \times 10^{-4}$  and  $5 \times 10^{-4}$  moles per 100 g latex were the critical levels with rapid changes in properties. There was no effect of fatty acid soap on MST on matured latex.*

**Keywords:** ammonium laurate soap; NRL; MST; conductivity; viscosity; foaming

Stability of the latex which is a unique property has been the major problem when latex is subjected to different mechanical actions. The chemical constitution of ammonia-preserved natural rubber latex (NRL) after storage differs considerably from that of the fresh NRL. The overall concentration of ions present in the aqueous phase tends to increase with the storage time<sup>1,2</sup>. Long chain fatty acids (FA) which are contributing to the stability in NRL develop gradually with time and attain to a maximum and tend to become constant at a stage. There can be different changes in the latex system during this period referred to as maturation.

It had long been known that FA can influence the membrane surrounding the rubber particle and hence many efforts have been carried out to study the effect of FA soaps on latex mechanical stability<sup>3-6</sup>. NRL flourishes under tropical conditions. Temperature, rainfall and soil fertility could affect the growth of the rubber tree. Climatic conditions of the area, clone, seasonal effects, age and state of health of the tree has a profound effect upon the character and yield of latex. Low quality latex obtained from rubber trees grown in cold climate and highly ionic soil conditions are known to have poor properties. However, explicit data on property variation of low

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quality latex was not available in literature to community and only a small number of investigations have been carried out. Previously reported results<sup>3</sup> revealed that addition of small amounts of potassium fatty acids could considerably enhance the mechanical stability time (MST). Although the fatty acids can increase MST in latex, it is apparent that it could cause some other problems in latex such as foaming, thus creating poor properties such as thinner walls and pin holes in dipped products.

This study was undertaken in view to fulfill the requirements of explicit data and to get a better understanding of properties on control addition of commercially available ammonium laurate soap. Further efforts were taken to analyze the effect of ammonium laurate soap level on foaming and possibility to reduce foaming with the introduction of an antifoaming agent. The effect of anti foaming agent on conductivity was also investigated.

## EXPERIMENTAL

### Materials

For the purpose of this investigation, low ammonia tetramethylthiuram disulfide preserved (LA-TZ) low quality concentrated NRL were used. They were collected from a leading latex manufacturer as one whole batch. The principal latex characteristics are shown in *Table 1*.

The ammonium laurate soap was prepared as an aqueous solution by neutralizing lauric acid with ammonium hydroxide. The ammonium hydroxide was of general purpose reagent supplied by Aldrich while lauric acid was a commercial grade reagent. Ammonium laurate was prepared as a 10% (w/v) solution. pH of the final soap solution was 10.0. Other materials used in this work were of analytical grade wherever possible.

TABLE 1. INITIAL VALUES OF PROPERTIES OF NRL USED

Property	Laboratory tested data
MST <sup>a</sup> (s)	25
KOH <sup>b</sup> number	0.85
VFA <sup>c</sup> number	0.071
TSC <sup>d</sup> (%)	59.05
DRC <sup>e</sup> (%)	57.5
Alkalinity	0.2
Viscosity (cp)	59.8

<sup>a</sup> Mechanical stability time.

<sup>b</sup> Potassium hydroxide number.

<sup>c</sup> Volatile fatty acid.

<sup>d</sup> Total solid content.

<sup>e</sup> Dry rubber content.

### Preparation of Natural Rubber Latex Samples with Different Soap Levels

Concentrated natural rubber latex was first strained through a wire mesh to remove any coagulum. Part of the NRL was then divided into seven portions. Required amounts of the stock ammonium laurate were added to these samples and corresponding molar levels per 100 g of NRL were obtained. Latex samples were prepared according to the soap concentrations given in *Table 2*. Each sample was placed in an air-tight plastic container having the same capacity. These samples were then stored under room temperature at  $(29 \pm 1)^\circ\text{C}$  for 3 days to allow equilibrium. Each sample was monitored for variation with soap concentration in MST, viscosity, conductivity, foaming height (FH) and potassium hydroxide number (KOH number). Sample A without added soap was the control sample.

### Preparation of Samples to Investigate Phenol Behaviour on Latex Base

The effect of phenol upon NRL properties was assessed as follows. Remaining NRL was

divided into two portions.  $0.84 \times 10^{-4}$  moles of soap were added per 100g of latex to one portion. Sufficient phenol was added from 10% phenol solution to one latex sample containing no added soap, and the other having  $0.84 \times 10^{-4}$  moles of added soap per 100 g of NRL. They were then labeled as H and J respectively. These samples were stored under room temperature at  $(29 \pm 1)^\circ\text{C}$  for 3 days to allow equilibrium before properties were investigated. Then the effect of phenol upon MST, conductivity and foaming height were investigated upon maturation for 5 weeks at one week intervals.

### Determination of Properties

Mechanical stability time was determined with 55% TSC at  $35^\circ\text{C}$  by means of a Klaxon MST test apparatus operating at 14,000 r.p.m. conforming to *ISO 35:1995[E]* procedure. KOH number was determined at room temperature and 30% TSC content by means of a combined apparatus system containing a pH meter, electrode, and magnetic stirrer. The test was carried out according to *ISO 127:1995[E]* procedure. Conductivity was determined at  $25^\circ\text{C}$  by means of a conductivity

TABLE 2. SAMPLES PREPARED TO INVESTIGATE PROPERTY VARIATION WITH SOAP CONCENTRATION

Sample Code	Soap Concentration in moles/100 g of NRL
A	No added soap
B	$0.5 \times 10^{-4}$
C	$1.4 \times 10^{-4}$
D	$4.2 \times 10^{-4}$
E	$5.0 \times 10^{-4}$
F	$8.01 \times 10^{-4}$
G	$14.01 \times 10^{-4}$

meter. Viscosity was determined at 27°C by means of a Brookfield viscometer according to *ISO 1652:1985(E)* procedure. TSC, DRC, alkalinity, and VFA number were determined in accordance with *ISO 124:1992*, *ISO 126:1974*, *ISO 125:1990*, and *ISO 506-1974 [E]*, respectively. FH was determined by the MST apparatus and a scale graduated in mm. Laboratory test data in *Table 1* are properties of NRL immediately after collection from the tree and concentration. All the properties with different soap levels are then compared with respect to these initial values.

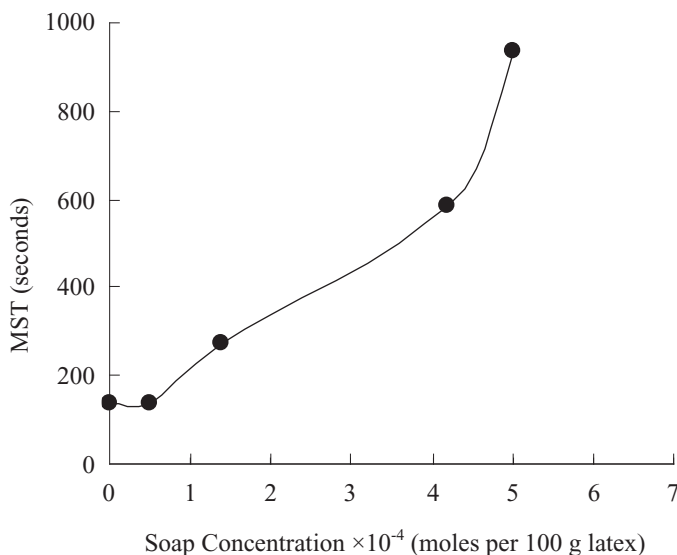
## RESULTS AND DISCUSSION

### Prevalence of Physical Properties over Level of Soap

Among the physical properties investigated, MST and FH were affected by the level of soap. *Figure 1* illustrates the change in MST as a function of soap level at three

days maturation after soap addition. Results apparently showed that very small amounts of ammonium laurate soap can produce considerable enhancements of mechanical stability of low quality NRL.

Effectiveness of ammonium laurate soap levels in increasing mechanical stability of NRL is very high. At the level of  $1.4 \times 10^{-4}$  and above, soap levels offered enhanced MST values by factors of about 2, 4.3 and 6.9 respectively indicating the influence of added soap on MST. Within the investigated soap levels, more rapid rate of increment in MST was observed between  $4.2 \times 10^{-4}$  and  $5.0 \times 10^{-4}$  levels. Results clearly showed that, in addition to lipid hydrolysis taking place in the NRL, added soap has enhanced the rate of adsorption and the additional adsorption at the rubber interface, displacement of naturally occurring proteins, which are relatively poor mechanical stabilisers compared with FA soaps as reported by Pendle<sup>7,8</sup>. Soap anions already



*Figure 1. Effect of ammonium laurate soap level on Mechanical Stability of LA-TZ latex concentrate.*

present having long alkyl chains cohere in clusters or islands<sup>3</sup> and therefore the effect of enhancing MST is less. Added soaps of intermediate alkyl chain length are strongly adsorbed at the interface and mix with the adsorbed fatty acid anions, which are already present in ammonia preserved NRL and cause the islands to disperse. Ammonium laurate being a soap of an intermediate alkyl chain may have strongly adsorbed at the rubber water interface by displacing some proteins that are weak mechanical stabilisers and mixed with indigenous soap ions. Its sufficiently short chain length may have disrupted the coherence of clusters of indigenous soap anions and dispersed them. Dispersion of indigenous soap islands by mixing have resulted in increasing repulsive energy between particles and thereby offering profound enhancement in the MST values. Reduction in the lateral cohesion of the indigenous soap islands may have a large effect upon rate of addition of soaps to the rubber particle by clearing the path to approach hindered weak proteins and their displacement. This phenomenon may be a dominating factor on enhancing MST of samples. Explanation for the rapid increment of the MST between  $4.2$  and  $5 \times 10^{-4}$  may be due to the attainment of critical micelle concentration of soap in the medium.

*Figure 2* illustrates the variation in viscosity of latex upon soap levels at three days maturation after soap addition. Viscosity describes the fluid's resistance to flow and results showed that reduction in the viscosity was brought about by addition of soap molecules to latex samples. Reduction may have been caused by distorting the original structure in solution<sup>9</sup>. As a result of soap addition, the randomly adsorbed foreign soap molecules may have brought about this by displacing protein at the surface of the particle changing its size and shape.

Conductivity variation upon soap levels at three days maturation after soap addition is demonstrated in *Figure 3*. According to the results, conductivity has increased rapidly at the initial stage and tends to become constant after a certain soap level. Verhaar<sup>10</sup> has reported the influence of hydrolysis in increasing conductivity upon storage. Chin<sup>6</sup> has confirmed this phenomenon with the aid of his slowly increased conductivity results upon storage.

Conductivity is a composite quantity attributable to overall ionic strength, basically nature and concentration of all dissolved ionic species. Surface-active substances in the medium may be present in a monomolecular form as well as micellar, whether or not these substances are ionized. Contribution from electrophoretic mobility of the particle is usually assumed to be negligible<sup>11</sup>. Contribution from the surface can be ignored, as rubber particles do not conduct electricity. Therefore, dissolved ions in the aqueous phase are attributable for the conductivity. According to *Figure 3*, conductivity increased up to 8% and tends to become constant after the level of soap reaches  $5.0 \times 10^{-4}$ . Results suggest that increased ionic strength of the aqueous phase brought about by added soap anions and their equivalent cations with respect to the level of soap has contributed to the rapid increase in ionic strength.

*Figure 4* illustrates the variation of FH on different levels of soap. According to results, FH rapidly increases with increasing levels of added soap. A minimum soap level employed has no effect. Pattern of variation of the results show that rather small soap levels can significantly increase foaming in latex.

Variation is almost gradual and rapid increase was observed between  $4.2 \times 10^{-4}$  and  $5.0 \times 10^{-4}$ . Results of the FH measurements apparently indicate the broad correlation of

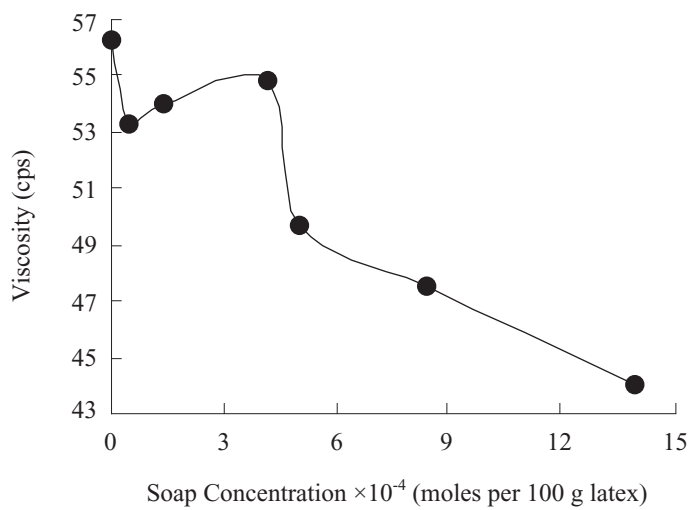


Figure 2. Effect of ammonium laurate soap level on Viscosity of LA-TZ latex concentrate.

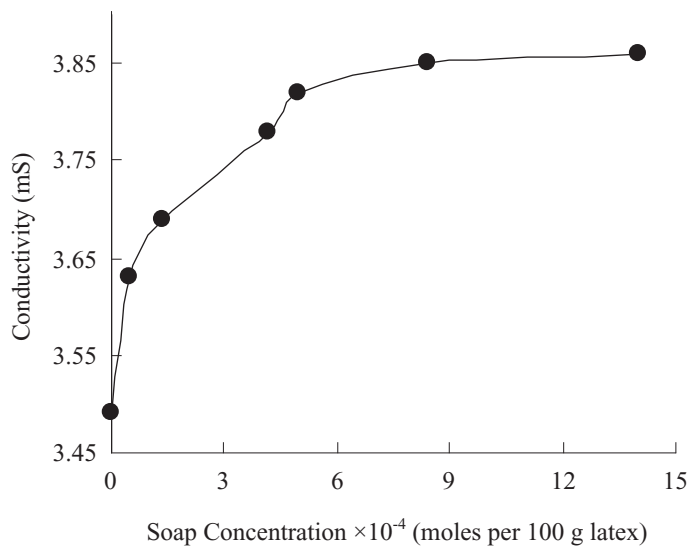


Figure 3. Effect of ammonium laurate soap level on Conductivity of LA-TZ latex concentrate.

foreign (added) soap on increasing foaming in NRL. In general  $1 \times 10^{-4}$  moles of soap approximately increase FH by 2 mm. Although the soap addition is a favourable feature for the MST, in the technologist's point of view its deleterious effect upon excessive addition can cause remarkable failures in the industry.

### Prevalence of KOH Number over Level of Soap

Variation of KOH number on soap level at three days maturation after soap addition is shown in *Figure 5*. KOH number was observed to increase with level of soap presumably due to many acid radicals formation.

However, at a certain soap level it tends to become constant, similar to conductivity variation. There is a direct correlation between conductivity and KOH number irrespective of soap level and storage<sup>12,13</sup> and this behaviour is observed here too. According to Bateman<sup>14</sup> many free acids, phosphoric acid, amino acid, oxalic acid, succinic acid, *etc.* have been reported to be present in latex serum. Results showed that the rate of KOH number increment was rapid between  $4.2 \times 10^{-4}$  and  $5.0 \times 10^{-4}$ . Explanation for this rapid increment can be related to the rapid increment of acid radicals upon addition of soap to the medium. This additional increment in increasing ionic strength of C-serum may have contributed to the rapid increase in KOH number. However, beyond this level, excess soap molecules in the medium tend to aggregate in micells thus inhibiting ionization in the medium and the medium becomes saturated with soap. Therefore, it offers constant number of acid radicals and is favourable to become constant. Inference that can be drawn from this is that soap molecules that rest in the ionized form in the medium are complementary to KOH number.

### Behaviour of Phenol on Latex

*Figure 6* illustrate the variation of MST in the presence of phenol at different storage times. Results showed that MST of all three samples including the control sample H and sample J vary in a similar pattern. Gradual increase in MST up to 3 weeks followed by gradual decrease was observed. It followed that there was neither reduction nor enhancement in MST upon phenol addition. Although soap itself increases MST, its combined effect with phenol diminishes the enhancement in stability.

Markwood<sup>15</sup> has reported that phenol has the ability to alter the surface tension of the soap solution. Results showed that the phenol has some direct effect upon added soap molecules. The action of soap depends chiefly upon its action as a dispersing agent in enhancing stability of dispersion. Hence, stability of the latex may be destroyed by the addition of a substance, which converts the dispersing agent into another substance.

Action of the soap may be broken up by adding an acid to form a salt of the added acid<sup>16</sup>. Phenol being a weak acid may have formed the ammonium salt of the phenol and the free acid of which the soap was originally the ammonium salt. This results in inhibiting the ability of added soap molecules to stabilise the rubber particle. By altering the surface tension of the soap solution, phenol has therefore inhibited the action of added soap molecules thereby inhibiting the additional enhancement in MST. Only improvement in MST is by indigenous soap molecules.

*Figure 7* illustrates the variation of conductivity in the presence of phenol at different storage times. Results showed that conductivity of all four samples including the control sample vary in a similar pattern. There is

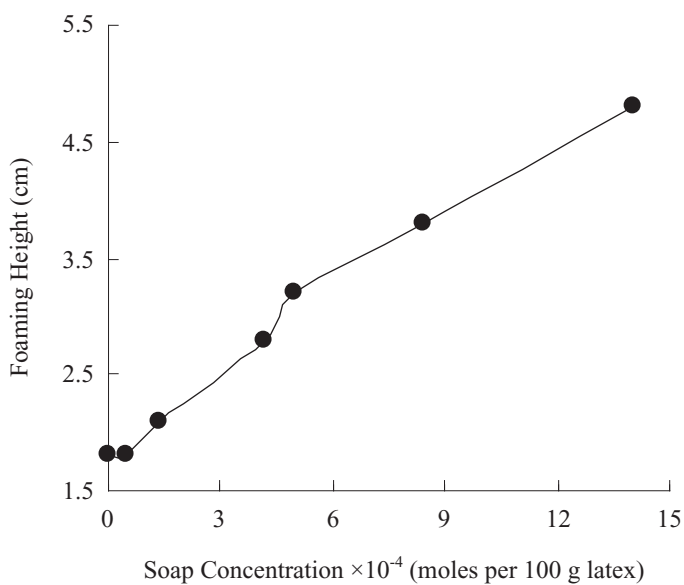


Figure 4. Effect of ammonium laurate soap level on Foaming Height of LA-TZ latex concentrate. (after 60 seconds stirring)

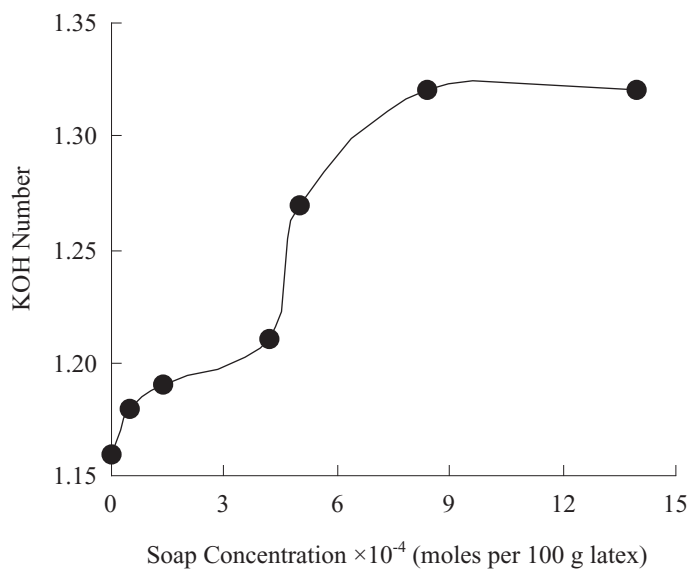


Figure 5. Effect of ammonium laurate soap level on KOH Number of LA-TZ latex concentrate.

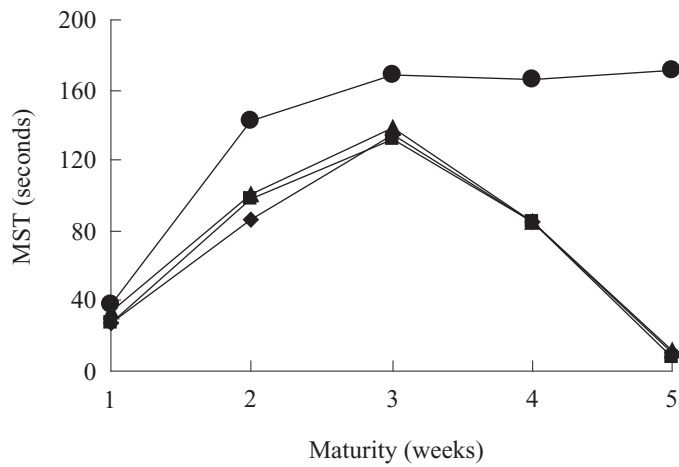


Figure 6. Effect of Phenol upon the MST of NRL in three different latex samples namely ▲ No added soap; ■ : Phenol added; ◆ Combination of Phenol & Soap and ● only soap added at five weeks of maturation.

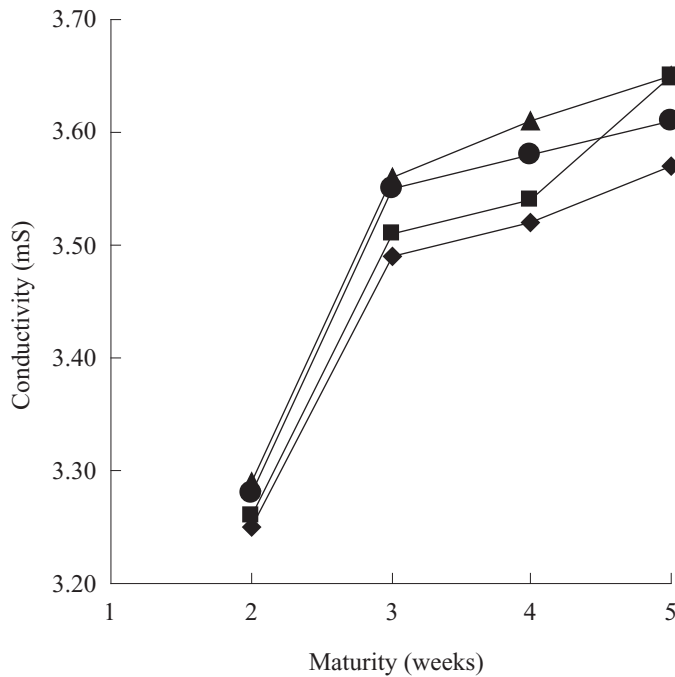


Figure 7. Effect of phenol upon the conductivity of NRL in three different latex samples namely ▲ No added soap; ■ : Phenol added; ◆ Combination of Phenol & Soap ● soap added at five weeks of maturation.

no significant effect of phenol and combination effect of phenol and soap on conductivity. This indicates that phenol does not contribute to the ionic strength of the medium and tends to bond with soap molecules rather than ionizing in the medium. Pattern of variation in conductivity follows in agreement with the explanation of lipid and protein hydrolysis.

Figure 8 illustrates the variation of foaming height in the presence of phenol at different storage times. Results show that phenol has certain effects upon FH. Phenol has the ability to alter surface tension of the soaps because of its acidic nature. Phenol has combined with added soaps and formed a corresponding salt, thereby inhibiting the soap action. Therefore foaming has reduced to a certain extent. In a sample with only phenol in the medium, phenol has formed a salt with free indigenous soap molecules, thereby reducing foaming

height. The sample with added soap molecules showed the highest foaming during storage but tends to be constant after a certain time period similar to MST.

#### Ammonium Laurate Addition after Maturation

Concentration of  $5.0 \times 10^{-4}$  moles of soap per 100 g of latex was added to 4 weeks matured control latex and further matured for one week to attain to equilibrium. MST was investigated at 5 day intervals. Results revealed that there is no enhancement in MST and remained as an almost unstable medium. Due to the absence of foreign soap molecules in the medium, destabilisation of latex begins after 3 weeks of maturation. Protein hydrolysis begins within 2-3 weeks maturation offering ions and increasing the ionic strength of the medium.

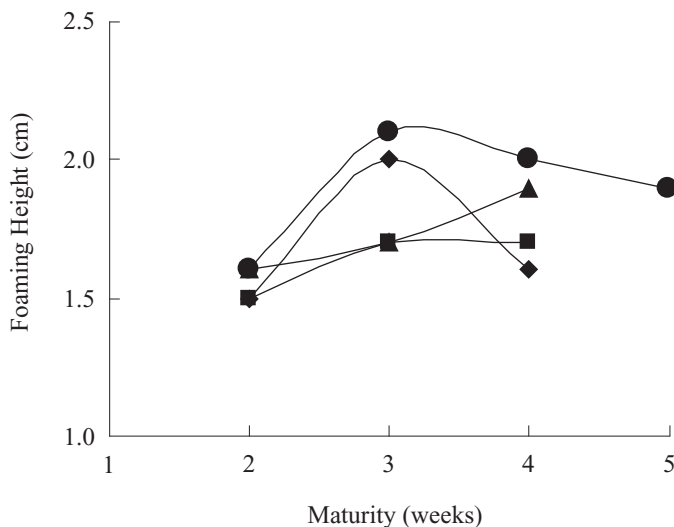


Figure 8. Effect of phenol upon the Foaming Height of NRL in three different latex samples namely ▲ No added soap; ■ : Phenol added; ◆ Combination of Phenol & Soap ● soap added at five weeks of maturation.

Ultimate compression in the electrical double layer brings particles more closer causing destabilisation.

Results support the fact that addition of soap after attaining the latex to complete destabilisation is not effective as enhancers of mechanical stabilisers. Protein hydrolysis may have changed the outer shell of the rubber particle to an extent where it inhibits the soap ion adsorption on the surface of the particle. Generally, soap adsorption takes place with displacement of weakly surface-active proteins and not at the vacant sites<sup>7</sup>. Furthermore, the process of adsorption is normally reversed by some other chemical substance that will react with the adsorbed substances<sup>17</sup>. Certain substances formed during the protein hydrolysis may have desorbed the part of adsorbed indigenous soap ions from the surface.

#### CONCLUSIONS

The work and results reported in this paper suggests that large increases in mechanical stability can accompany the addition of small amounts of ammonium laurate to low quality NRL. Furthermore, the minimum level of soap to create substantial enhancement in MST without giving rise to potential problems in compounding and processing has been identified. There is a critical soap concentration in the latex giving rapid increase or decrease in properties. It is also apparent that foreign soap increases the foaming in latex. Phenol reduces foaming but has a detrimental effect upon MST.

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