Slide 1:

I'd like to thank the IRE 2013 for the invitation, and I' like to acknowledge my co-authors: Mr. M. Clark, Mr. G. Narayanan, Mr. Joseph John and Dr. R. K. Matthan.

Slide 2: Model of rubber latex particle / depiction of rubber polyisoprene chain crosslinked by sulphur

NR latex particles in a matured commercial latex concentrate are stabilized by charged groups derived from proteins, long-chain fatty acid soaps and polypeptides adsorbed on the particle surface. The colloidal stability of the latex is extremely sensitive to pH as well as to the ionic environment of the dispersing medium. Previous work on particle microelectrophoresis has shown that the charge on the particle surface is derived mainly from carboxylic groups of long chain fatty acids (ca. 86%). The rubber particles are surrounded by protein anions and are negatively charged.

SLIDE A-

The protein sheath, which may be amphoteric in nature, around the latex particle is conjectured to facilitate the movement of curatives, usually carbon-, sulfur-, and nitrogen-containing materials, into the latex particles by providing an intermediate transport mechanism from the water phase to the rubber phase. The removal of the non-rubbers in Aluminum Hydroxide treated NRL (from here on out, I will refer to it as ALOX latex) slows down the maturation process, hence translating into a longer "pot life."

SLIDE B-

Natural rubber has been the most studied, and here vulcanization is thought to occur as follows. First an active sulphurating agent is formed, through the reaction of the S8 sulphur molecule with the accelerator (such as ZDBC, ZDEC and ZMBT). This reaction is facilitated by the presence of ammonia or other amines. The active sulphurating agent can then react with a rubber molecule to insert a short sulphur chain into the polymer chain, forming what is called a rubber-bound intermediate. This rubber-bound intermediate then can react with other rubber molecules to form the initial cross-linked network.

At the same time, the residues from the accelerator can react with zinc oxide (an activator) to regenerate the accelerator, which can then continue the reactions. We are not at the end of the process yet, however. This initial cross-linked network continues to react in various ways. The sulphur chains can break and reform, leading to crosslink shortening, lengthening or additional crosslinks being formed.

Increasing crosslink concentration produces the following effects:

- <u>Static and dynamic modulus increment</u>— the requiring movement in gloves for example
- <u>Elasticity or permanent set decreases</u>—max cross links make more brittle
- <u>Tensile strength increases and then decreases</u>
- <u>Tear strength increases and then decreases</u>
- <u>Elongation at break increases and then decreases</u>
- <u>Hysteritic energy loss decreases</u>

With that said it is up to individual manufacturers to determine the optimal conditions to maximizing physical performance of their end product. ALOX latex, by removing non-rubbers, offers a consistent raw material as opposed to untreated NRL.

Slide 3: The four major zones in NRL and their function

It has been known for a long time that Natural rubber (NR) latex extracted from the Hevea brasiliensis is a polydisperse cytoplasm system containing 30-45% weight of rubber molecules (cis-polyisoprene), 4-5% weight of large variety non-rubber constituents such as protein, lipids, carbohydrates and sugar and 50% of water. Many of these constituents are dissolved in the aqueous phase of the latex, others are adsorbed at the surface of the rubber particles and some are suspended in the latex. The latex composition usually depends on the season of the year for the extraction and age of the tree.

The major rubber particle membrane protein is a 14KD polypeptide known as 'the rubber elongation factor'. However, this latex protein along with a 30KD protein has been reported to be an important allergen in Type 1 allergic reaction.

ALOX latex has low content of non-rubbers, in virtue having low amount of both 14KD protein and choline compounds. However, it should not cause any effect to vulcanization as compounders still can opt to add other types of accelerators like ZDBC, ZDEC and ZMBT. As for anti-oxidant, it is best to add synthetic anti-oxidants as natural anti-oxidants will denature on storage. Therefore, vulcanization in ALOX latex is not affected by reduction in the amount of choline and 14KD protein.

To date, well over 100 production lots of ALOX latex have been produced. Interestingly, we and our customers have noticed numerous additional benefits from the ALOX treated process. For instance, the ALOX is adsorbing many of these non-rubber components, which are being removed from the latex during the centrifugation process. The results for the end products are illustrated in subsequent slides.

Slide 4: Aluminum hydroxide treated latex

The patented aluminium hydroxide treated process is dependent on the effective exchange of proteins from the field latex (FL) to insoluble ALOX. The FL contains several non-rubber impurities coming from the Hevea brasiliensis rubber tree such as lutoids, lipids, Frey Wyssling particles, carotenoids and of course numerous proteins.

The ALOX is delivered to the FL in the form of a slurry containing a proprietary blend of additives designed to liberate non-rubbers attached to the rubber particle, displacing them into the aqueous phase. Once in the aqueous phase, these non-rubbers, including proteins, are adsorbed to the ALOX. Since the ALOX is insoluble, this newly formed complex is removed from the latex during the centrifugation process. The resultant material has been commercially branded as Vytex NRL and contains significantly less non-rubber components than standard NRL and is much cleaner and whiter, making this an excellent choice material for several product applications which will be discussed in subsequent slides.

Slide 5: Property Comparison between ALOX Treated NRL and Standard NRL

Every production lot of ALOX latex produced is tested to ensure ISO compliance. Additionally, ALOX latex is independently tested for antigenic and total protein using the ASTM D 6499-07 test method for antigenic protein and ASTM D5712-10 modified Lowry test method.

As you will see from the results listed at the bottom, ALOX latex is quite comparable to standard latex with the exception of having a lower NRC and significantly less antigenic and total protein. All colloidal properties are within ASTM specifications. It is important to note that the process is flexible and can be modified to accommodate special product applications.

Slide 6: Condom Burst Analysis of ALOX latex Performed by Company A (Richter Rubber)

To date, condoms made from ALOX latex have received the lowest and only claim of less than 2 ug/dm2 of antigenic proteins by the US FDA. Several manufacturers have upgraded to using ALOX latex for condom production and noted these condoms are more transparent, less odorous and contain less nitrosamines than condoms made with standard latex. The improved rubber to non-rubber ratio in

ALOX latex results in improved dynamic properties (resilience & rebound) translating into high quality condom products.

The results from a manufacturer using ALOX latex illustrated on this slide confirm that the ALOX latex performs within the acceptable limits of the ISO 4074 standards.

Slide 7: Physical properties of Examination Gloves Made from ALOX Treated NRL and Standard NRL-

The physical properties of ALOX latex were compared to properties of standard latex manufactured by company B. The removal of non-rubber components in ALOX latex led to higher initial tensile strength compared to gloves made from standard latex. Also the gloves made with ALOX latex had better elongation % compared to gloves made from standard latex.

Most noteworthy was the conclusion that gloves made from ALOX latex were MUCH softer and had significantly lower initial modulus. This feature can be contributed to the removal of non-rubbers in the ALOX latex thus allowing for greater movements with less effort required, making this the choice material for gloves being worn for long periods of time such as surgical gloves.

Slide 8: Compounding of ALOX and Standard Lattices

1 ALOX latex and standard Hevea CL60 was compounded using the same formulation as per in the slide. The dispersions used were carefully formulated without any casein addition to prevent misleading results for protein content.

2 The compounds were left for maturation and checked for their crosslinking density using toluene swell test at interval of 6 hours. Please refer to ***Slide Toluene Swell Analysis*** for the toluene swell data comparison.

Slide 9:

3 Once the toluene swell reached about 90%, both compounds were dipped.

<u>Results and Discussion:</u>

1 The toluene swell results shows that both ALOX latex compounds with 40 phr filler and 45 phr filler having almost similar cross link density and slower maturation compared to standard Hevea CL60. However, standard Hevea CL60 shows faster maturation and gloves need to be dipped within 30 hours after compounding.

2 The ALOX latex compounds need to be dipped within 42 hours after compounding and can be used within the span of 12 hours. But, standard Hevea CL60 has shorter dipping time span ie 6 – 8 hours after that, the compound overcured and cannot be used.

Slide 10: Physical Properties of Different Compounded Treated NRL and Standard NRL

3 In terms of physical properties, ALOX latex and standard Hevea CL60 with 40 phr filler have almost the same tensile strength. But, ALOX latex gloves felt softer due to higher elongation at break. Therefore, there is room for extra 5 phr filler to accommodate the absence of non-rubbers. Even with extra 5 phr filler, the elongation

at break results was higher than standard Hevea CL60 with 40 phr filler. Record of modulus at 300% elongation suggests that both ALOX latex compounds using 40 phr and 45 phr filler are still softer than standard Hevea CL60.

Conclusion:

1 The slower rate of cross linking in ALOX latex would benefit glove manufacturers in terms of longer shelf life of the compounds for longer span of dipping hours. As such, the manufacturer can use the compound for longer time compared to standard Hevea CL60 compounds.

2 Softer feel of ALOX treated NRL gloves and comparable physical properties even at 45 phr filler makes ALOX latex a better choice for cost saving approach. Addition of higher load of filler on ALOX treated NRL gloves can be done without any quality deterioration. This is because there is extra room in ALOX latex for more filler loading due to absence of non-rubbers.

Slide 11: Cost Analysis-

Vytex premium can be offset with the removal of non-rubbers being able to accommodate a higher filler loading. We put together this cost analysis knowing that 35 phr is the recommended fill load used by manufacturers. We tested at 40 phr for both standard and ALOX lattices. Looking at MRB at a point in time and adding for the 10%, 15%, and 20% as premium filler we held all other components at the same price and same source raw material. This does not take into account the added benefit of reduced leaching and rinsing as shown in previous papers.

In other words using the standard 35 phr as a baseline and also comparing standard latex at 40 phr, this exercise shows that even at a 10, 15, to 20% premium over MRB, ALOX latex shows comparable pricing benefits in its worst case or slightly lower in others.

Slide 12: Quantitative Color Determination of Balloons

The color determination was performed using Hunter Color Lab colorimeter, where balloons made from ALOX latex were tested against balloons made using standard latex by a large American manufacturer. The test was very subjective and could differentiate the L, a, b values between the 2 variants. All tests were performed by LGM (Colorimetric study at Malaysian Rubber Board).

In the highlighted section Δ a refers to values on the red-green axis. The positive numbers in the orange and red rows show a stronger red color, thus a more intense orange color as well. Similarly, the negative number in Δ a in the green row indicates a more vibrant green.

In Δ b, referring to the blue-yellow axis, the positive differential shows the balloon to have a stronger yellow color. Also, the combination of a higher lightness axis difference coupled with a negative Δ b shows a clearer less yellow plain balloon.

Slide 13: Lab Color Analysis of Balloons

These results are graphed for illustration

Slide 14, 15, 16:

Actual balloons made with Vytex compared to balloons made from regular NRL

Slide 17: Balloon Gas Retention for Helium and Air

Balloons made from ALOX latex were compared to balloons made from standard latex. Due to the removal of the non-rubber components in ALOX latex, these balloons retained air and helium much longer compared to standard latex balloons. We believe this is due to tighter rubber particle integration thus creating better barrier properties.

Slide 18: Conclusions