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Green ammonia-free preservation and stabilization of natural rubber liquid latex

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Executive summary

Current methods to avoid decomposition and coagulation of natural rubber liquid latex involve the use of additives, which include ammonia, that are harmful to the environment and to the people handling the material. A new technology to preserve and stabilize natural rubber liquid latex in an acidic environment without the need of harmful chemicals was developed. Rubber and products that are manufactured using this new green technology have superior mechanical properties and have been shown to be hypoallergenic. This new green latex has been used in the creation of adhesives that outperform high-performance industrial adhesives currently in the market.

Introduction

Of the 14 billion kilograms of natural rubber produced worldwide every year, 12 percent ends up in products manufactured from natural rubber concentrated liquid latex such as those resulting from dipping processes, adhesives, foams, etc. When tapping the *hevea brasiliensis* tree, an incision is made on the bark of

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the tree, severing laticiferous cells, which release a white and opaque liquid latex. The natural rubber liquid latex is composed approximately of 35 percent by weight rubber particles, 5 percent by weight of other solids, such as proteins, sugars, amino acids, lipids, and minerals, and 60 percent water. The sugars, proteins, amino acids, and lipids render the liquid latex susceptible to rapid decomposition by bacteria and other living organisms when it encounters air the moment it is extracted from the tree (**Fig. 1**). The onset of putrefaction triggers an unwanted coagulation process, which renders the latex challenging to handle and process. Hence, the natural rubber producer currently uses chemicals, such as ammonia, tetramethylthiuram disulfide (TMTD), and zinc oxide (ZnO) to stabilize and preserve the liquid natural rubber latex. Once these chemicals are added, the latex no longer decomposes, and it remains in a stable flowable condition (**Fig. 2**).

However, ammonia, TMTD, and zinc oxide are harmful to the environment and the people handling the preserved and stabilized natural rubber liquid latex. The presence of these chemicals, particularly the strong smell of ammonia emanating from the liquid latex, does not go unnoticed in the field, processing plant, manufacturing facilities and even in the final product. In the preface of his 2021 book, Empire of Rubber[1], Gregg Mitman writes that during a visit to the Firestone facilities in Liberia, the "smell of ammonia in the processing plant can be overpowering, as I learned when I too carelessly bent down to sniff the fast-moving latex flowing through the plant and was almost knocked unconscious." He also observed how the handling of ammonia without appropriate safety standards and precautions often led to injury among the rubber tree tappers and processors.

Additionally, the impact of ammonia on the environment is also a major concern, and several countries are regulating their concentration in the wastewater from manufacturing plants. However, these limits remain very difficult to achieve, especially for small-scale rubber growers and processors, which constitute the vast majority of rubber producers in several countries.

Green stabilization and preservation of latex in acidic media

Two completely green technologies to stabilize and preserve liquid latex in acidic media have been developed[2,3,4]. The first technique employs 2 percent by volume dodecyl benzene sulfonic acid (DBS) to stabilize and preserve liquid latex. It is hypothesized that the DBS reacts with a tripeptide found in the liquid latex known as glutathione, resulting in a molecule referred to as glutathione dodecylbenzenesulfonate (**Fig. 3**). This molecule stabilizes and preserves the liquid latex. Similarly, a second method uses a combination of 1 percent by volume ethoxylated tridecyl alcohol, which stabilizes the colloidal liquid latex suspension, and a 0.4 percent by volume of a 50/50 hydrofluoric acid/water solution, which acts as a preservative. Both approaches have proven to preserve and stabilize natural rubber field latex as well as centrifuged latex for at least four years, a period considerably longer than those obtained with the traditional ammonia-based techniques.

The counterintuitive use of acidic environments is the main

Fig. 1: Natural rubber latex architecture before the onset of putrefaction and coagulation process.

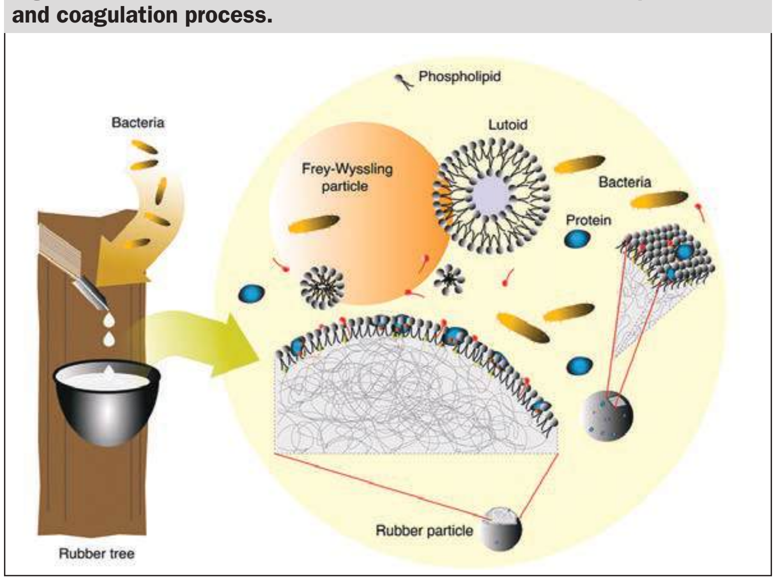


Fig. 2: Ammonia stabilized natural rubber latex architecture.

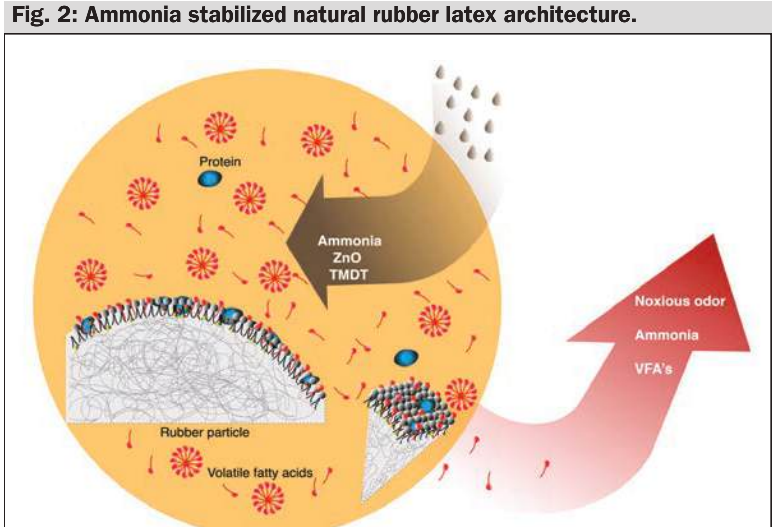


Fig. 3: DBS stabilized and preserved natural rubber latex architecture.

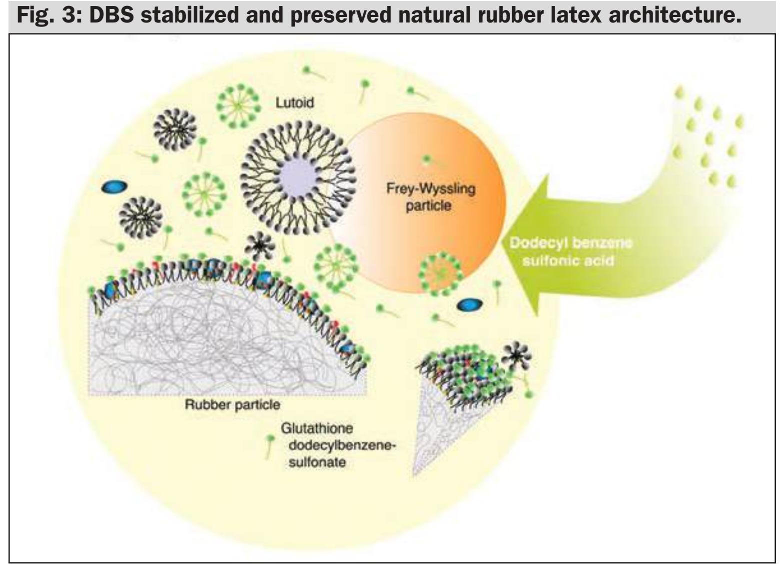
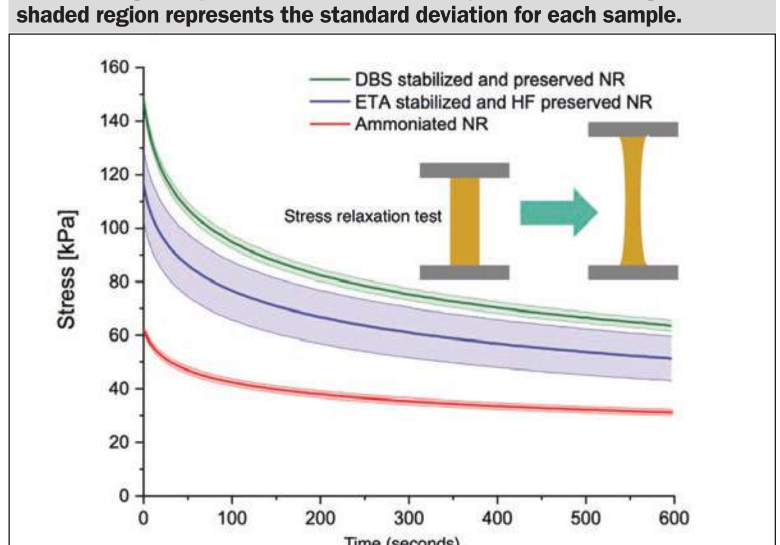


Fig. 4: Results from the relaxation tests with an imposed 30% tensile strain on a rectangular specimen. The solid lines represent the average while the shaded region represents the standard deviation for each sample.



The authors

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novelty of these ammonia-free recipes for the stabilization and preservation of liquid latex. Traditionally, it is assumed that alkaline conditions, like those created by ammonia solutions, are ideal for maintaining latex stable, whereas acids such as sulphuric and formic acid are used to promote its coagulation process. Although ammonia successfully preserves and stabilizes the natural rubber latex, it does so at the expense of the proteins and many living organisms in charge of enhancing mechanical performance and resulting in large quantities of allergenic proteins. Hence, the novel ammonia-free preservation and stabilization technique results in natural rubber products, such as adhesives, with superior mechanical properties. **Fig. 4** presents stress relaxation curves for solid rubber obtained from the ammonia-free preservation and stabilization technique, as well as from ammoniated latex.

Electrophoresis and ELISA tests also show that the ammonia-free preservation and stabilization techniques result in a 65 percent reduction of allergenic proteins from those encountered with ammoniated latex.

High-performance solvent-free adhesives

The novel environmentally friendly ammonia-free natural rubber latex stabilized and preserved with ethoxylated tridecyl alcohol and hydrofluoric acid was used to create an adhesive with superior mechanical properties and ease of handling[5]. The green formulation makes use of natural bio-additives, such as cellulose and collagen, without the use of organic solvents. The new ammonia-free adhesive outperformed common heavy-duty footwear and flooring adhesives. **Fig. 5** compares peel test results of leather pieces bonded with the green solvent-free adhesive to an adhesive made of ammoniated natural rubber latex and two solvent-based adhesives. The results clearly show how the ammonia-free adhesive outperforms the commercially available adhesives. **Fig. 6** compares shear stress results between the ammonia-free natural rubber latex adhesive and a commercially available solvent-based carpet adhesive. The ammonia-free adhesive clearly outperforms the solvent-based adhesive.

The enhanced performance of the ammonia-free adhesive is likely explained by the ability of ammonia-free latex to support a molecular network involving phospholipids and protein molecules, which enhances the stability of the adhesive. Several more ammonia-free natural adhesives based on natural rubber latex are currently under development, which will form a new class of sustainable and environmentally friendly adhesives for high-performance applications.

Work is also underway to find appropriate formulations to apply the acidic ammonia-free hypoallergenic natural rubber liquid latex to the dipping process used in the manufacture of balloons, condoms and gloves.

References

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Fig. 5: A comparison of T-Peel strength test results for leather-based adhesives in accordance with ASTM F2265.

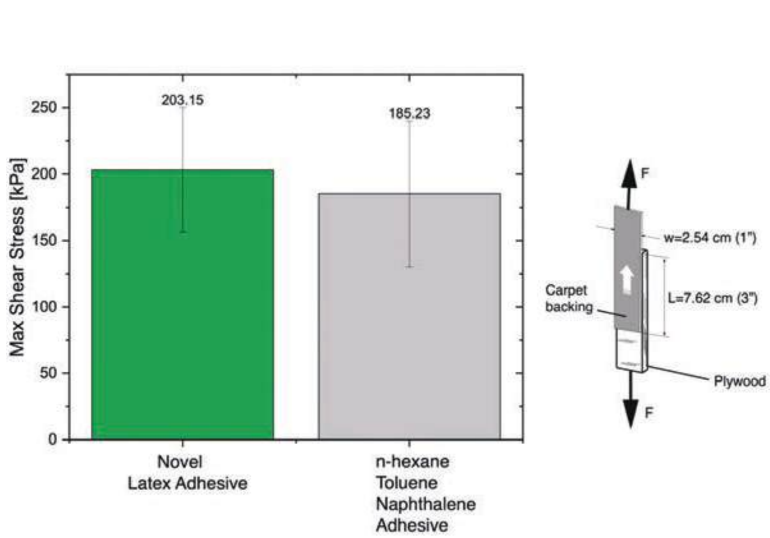

Fig. 6: A comparison in shear strength performance between the AF Latex bio adhesive and the traditional solvent-based carpet adhesive.