Environmentally friendly ammonia-free preservation and stabilisation of natural rubber liquid latex

Natural latex is the raw material that supplies about half of the rubber production worldwide. Latex is a fragile liquid which quickly decomposes in air shortly after its extraction from trees. Traditional means to avoid decomposition involve the use of additives, including ammonia, that are harmful to the environment and the people handling the material. A team at AFLatex Technologies in Portugal, led by Julio C Rodríguez and Professor Tim A Osswald, proposes two new routes to stabilising latex that don't require the addition of harmful chemicals. These treatments also make latex suitable for the creation of adhesives whose efficiency outperforms those of current high-performance industrial adhesives.

The rubber market has been steadily increasing in volume and value over time, reaching a global production of about 20 million tons in 2021, with projected revenues expected to be well over 70 billion US dollars by 2029. Rubber is an important material with a variety of practical and technological applications, from clothes and toys to medical devices and tyres for aircraft and cars.

Natural rubber constitutes about half of the world's total rubber consumption. It's an essential renewable resource and the most carbon-negative biopolymer. Natural rubber is obtained through the extraction and treatment of latex, a liquid sap produced by specific tree and plant species. Most of the latex is sourced from *Hevea brasiliensis*, the rubber tree, although over 2,500 varieties of trees and plants are capable of producing sap suitable for rubber manufacture.

COSTS OF CHEMICAL STABILISERS

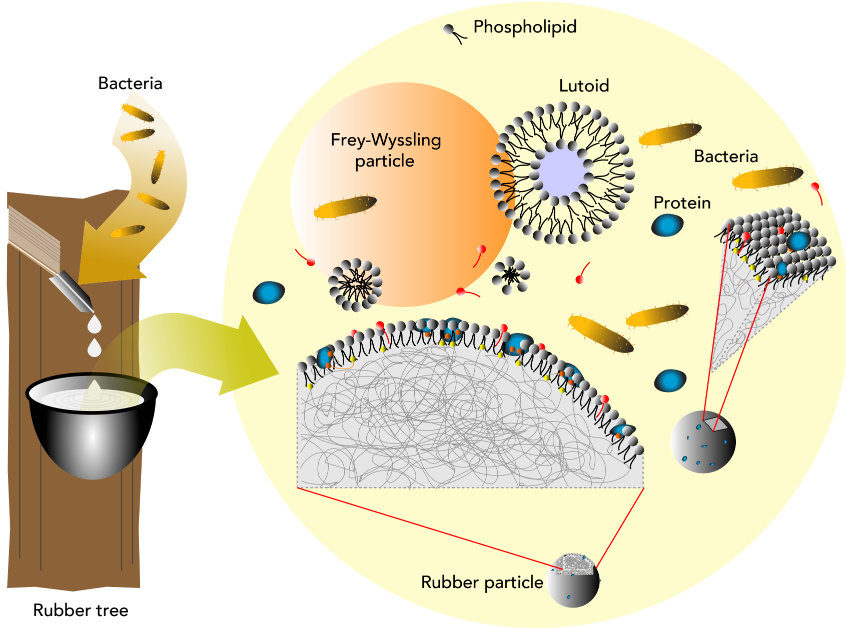
Liquid latex is composed largely of water (60% in weight), rubber particles (35%), and other solid particles, including proteins, sugars, amino acids, lipids, and minerals. The presence of this small number of solid particles makes latex susceptible to rapid decomposition, which is caused by airborne bacteria and other microorganisms. This process leads to putrefaction and coagulation, rendering latex unsuitable for handling and further processing. To avoid decomposition, natural rubber manufacturers are therefore forced to use chemical additives, such as tetramethylthiuram disulphide, zinc oxide, and ammonia. This keeps latex in a stable liquid phase for long enough to allow the removal of excess water and its conversion into raw rubber.

The addition of stabilisers to latex has significant consequences for the natural rubber manufacturing process. All common chemicals currently used to stabilise latex are harmful both to human health and to the environment. In particular, the strong and pungent smell of ammonia dissolved in liquid latex can often be perceived not only in processing plants and manufacturing facilities, but also in the final product. In his 2021 book *Empire of Rubber*, a shocking report of a visit to Firestone rubber facilities in Liberia, Gregg Mitman describes the dramatic effects of ammonia vapours on people working at these plants, remarking how a sniff from the fast-moving latex flow was sufficient to almost knock an adult unconscious. He also observed how the handling of ammonia without appropriate safety standards and precautions often led to injury among the rubber manufacturers – including, in some cases, blindness caused by the dangerous and corrosive chemical reaching their eyes.

The impact of chemical stabilisers on the environment is also a major concern, and several countries have recognised the need to regulate their concentration in 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.

ENVIRONMENTALLY FRIENDLY LATEX PRESERVATION

A team at AFLatex Technologies in Portugal, consisting of Professor Tim A Osswald, Julio C Rodríguez, German Pardo, Eric Adler, and Allen J Román, have examined why chemicals like ammonia act as efficient latex stabilisers, with the aim of proposing environmentally sustainable alternatives to the use of these dangerous chemicals.



Latex is susceptible to rapid decomposition, caused by airborne bacteria and other microorganisms.

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The liquid latex tapped from rubber trees is a colloidal suspension, with a density only slightly inferior to that of water, of three types of particles: rubber particles, Frey-Wyssling particles, and lutoids. Rubber particles are surrounded by a layer of phospholipids, which are elongated molecules with a hydrophobic end, pointing toward the rubber, and a hydrophilic end, in contact with the surrounding serum. Frey-Wyssling particles are larger and lower in number. They contain carotenoid, a dye molecule which imparts natural rubber its yellow colour. Lutoids are spherical particles containing an aqueous solution of sugars, amino acids, and proteins.

The addition of ammonia to latex stabilises the colloidal suspension by destroying the lutoids and the phospholipid molecules, forming volatile fatty acids, which contribute to stabilising the rubber particles. Ammonia also helps to preserve liquid latex by killing the bacteria responsible for its decomposition, provided this chemical is added to sufficiently high concentrations. However, the effects of ammonia and other common chemicals wane over time, and stabilised latex has a shelf life of about six months.

LATEX STABILISATION AND PRESERVATION IN ACIDIC MEDIA

The team of researchers have proposed two latex preservation and stabilisation methods that differ drastically from conventional approaches. They are completely ammonia-free and do not require other potentially hazardous chemicals such as tetramethylthiuram disulphide or zinc oxide. At variance with ammonia-based approaches, they exploit an acidic medium to preserve the latex after stabilisation.

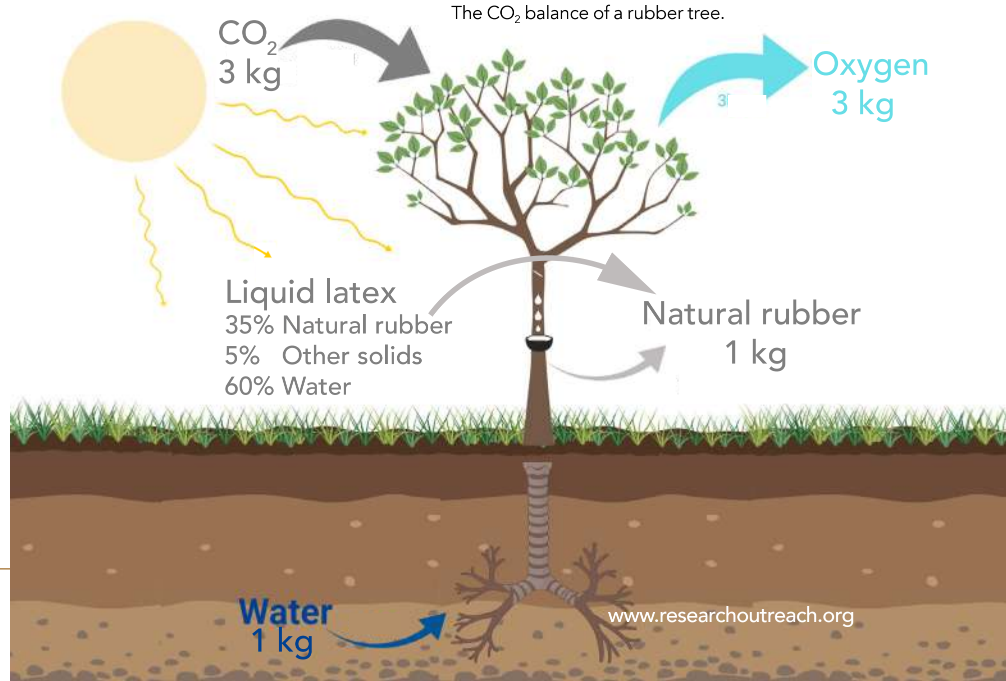
The first method employs dodecyl benzene sulfonic acid (DBS) to stabilise and preserve liquid latex, whereas the second method uses a combination of ethoxylated tridecyl alcohol, which stabilises the colloidal liquid latex suspension, and hydrofluoric acid, which acts as an efficient preservation agent. Both approaches can preserve natural rubber latex for at least four years, a period considerably longer than those obtainable following ammonia-based preservation routes in which a slow coagulation process is observed, leading to a gradual increase in viscosity.

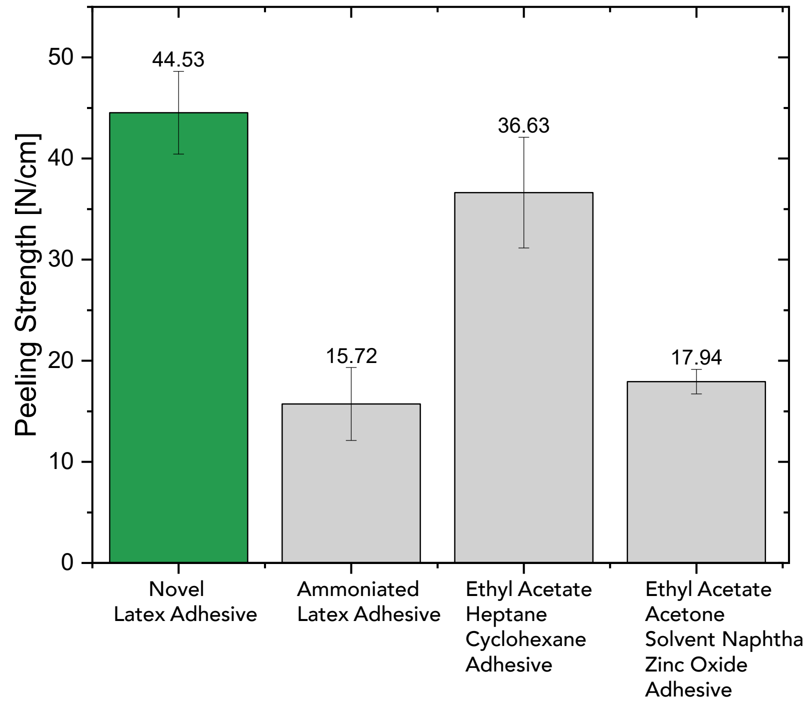
CHEMICAL PROCESSES IN ACIDIC LATEX

The use of acidic environments is the main novelty of the researchers' ammonia-free recipes for the stabilisation and preservation of liquid latex, and their success is, at first sight, counterintuitive. It's usually assumed that alkaline conditions, like those created by ammonia solutions, are ideal for maintaining latex stability, whereas chemicals such as sulphuric and formic acid are known to promote its coagulation and degradation.

The group has been able to provide an explanation for their surprising findings by carefully studying experimentally the balance of chemical reactions occurring in latex in the presence of acidic species. When DBS is used to stabilise latex, its reaction with a small polypeptide known as glutathione, which is naturally present

The CO_2 balance of a rubber tree.

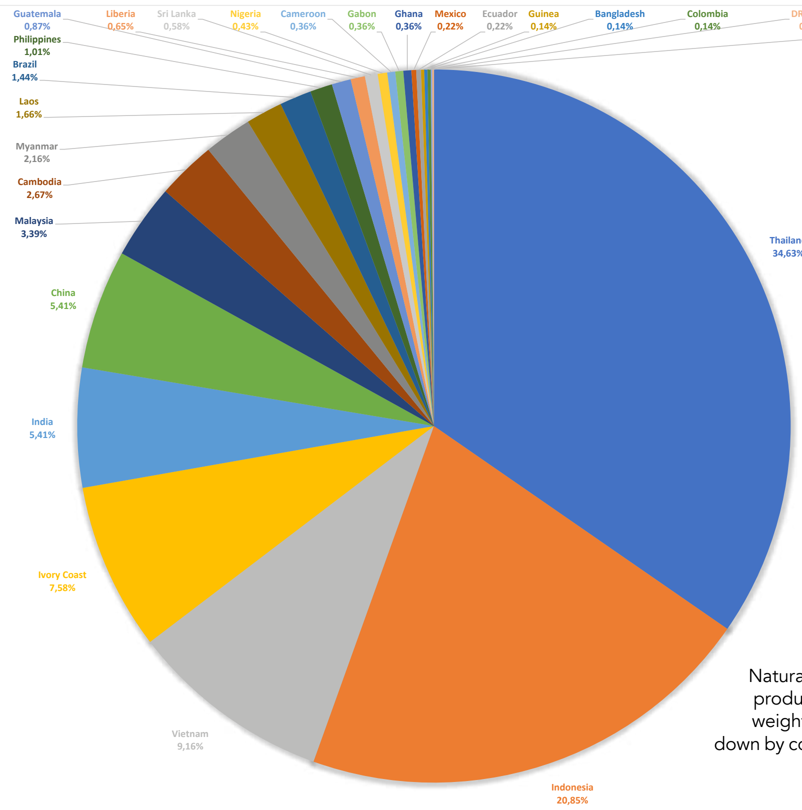




Comparison of an adhesive made with AFLatex Technologies' novel latex (left) with commercial environmentally unfriendly additives.

Ammonia-free adhesives have been shown to outperform common heavy-duty flooring and footwear adhesives.

in liquid latex, leads to the generation of glutathione dodecylbenzenesulphonate. This molecule acts as a surfactant that strengthens the phospholipid layer protecting rubber particles and enhances their stability. It is also an antibiotic, which



Natural rubber production by weight broken down by countries.

kills the bacteria responsible for latex decomposition and can preserve latex for long periods of time.

Similarly, ethoxylated tridecyl alcohol, which is used in the second approach proposed by the group, stabilises the colloidal liquid latex suspension. In this case, however, latex is still susceptible to putrefaction and decomposition. The addition of an aqueous solution of hydrofluoric acid and its reaction with glutathione generate a molecule known as glutafluora, which has strong antibiotic activity and prevents the growth of the bacteria that trigger decomposition.

HIGH-PERFORMANCE ADHESIVES

The use of natural rubber latex in the adhesive industry is rather limited, largely because of the poor resistance of this material to water and chemical attack. In addition, latex adhesives prepared using traditional methods contain ammonia, which makes them toxic and unsuitable for civil or industrial applications. Currently, most high-performance adhesives are solvent-based. This is also a source of serious hazard to human health and the environment, as organic solvents can be toxic and polluting.

The team at AFLatex Technologies have applied their ammonia-free method for natural rubber latex stabilisation and preservation based on ethoxylated tridecyl alcohol and hydrofluoric acid to create an adhesive with superior mechanical properties and ease of handling. Their formulation makes use of natural bio-additives, such as cellulose and collagen, and does not require organic solvents. This ammonia-free adhesive has been shown to outperform common heavy-duty flooring and footwear adhesives. Its enhanced performance is likely to be 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.

Behind the Research

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Research Objectives

The research team propose environmentally friendly latex preservation and stabilisation methods.

Detail

Bio

Professor Tim A Osswald is co-General Manager of AFLatex Technologies, Professor at the University of Wisconsin-Madison, co-director of the Polymer Engineering Center, Honorary Professor at the University of Erlangen-Nueremberg in Erlangen, Germany, and Honorary Professor at the National University of Colombia.

Julio C Rodríguez is General Manager of AFLatex Technologies, and Scientific Director of SOAN Laboratorios in Bogotá, Colombia.

Dr Allen J Román is Director of Science and Technology at AFLatex Technologies, former Chief Engineer and Graduate Student at the Polymer Engineering Center, and currently Post-Doctoral Researcher at Argonne National Laboratories in Chicago, USA.

Eric P Adler is Director of Finance of AFLatex Technologies, and CEO of Adler Financial in Madison, USA.

German Pardo is Director of Sales of AFLatex Technologies, and General Manager of SOAN Laboratorios in Bogotá, Colombia.

References

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AFLatex technologies

Personal Response

What inspired you to conduct this research?

" The inspiration for this work came from our collective love for the environment. Our collaborative team met for the first time at the XVI Rubber Technology Conference of the Latin American Rubber Technology Society (SLTC) in Querétaro, Mexico in 2019. Each of us brought our unique knowledge, from Rodríguez' chemical expertise and work on rubber stabilisation to Osswald's polymer engineering background and personal passion for the mysteries that surround natural rubber, seen first-hand in his hobby rubber tree farm in Colombia.

What are the main advantages of the ammonia-free natural rubber latex preservation and stabilisation methods over traditional approaches, and which technological fields will be most impacted by your discoveries?

The main advantage of our discovery is that by removing the cocktail of harmful chemicals that have been traditionally used in the processing of natural rubber latex, we not only protect the environment and the people involved in rubber processing, but we also produce a material with superior mechanical properties. In addition to adhesives, our technology has the potential to impact any product made from rubber latex and solid rubber, affecting the medical, automotive, athletic, and household industries. "