

AMMONIA-FREE, LOW-ODOR LATEX AND STABILIZED LATEX COMPOUNDS

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ABSTRACT

Latex compounds are multi-component systems comprised of particles of different natures dispersed in water. Under heat, chemical coagulation and mechanical shearing conditions, the stability of the latex compound relies on effective separation of these particles by various stabilizers. As a safe, low-odor, low-foam multifunctional stabilizer, CHAINGUARD™ DB effectively stabilizes latex concentrate, latex compound and resultant dipped goods against heat, chemicals and environmental aging. Detailed benefits include pH stabilization, lump reduction, surface-tension reduction, improved syneresis control, reduced pinkish of natural latex and improved glove-palm-to-fingertip thickness uniformity. When used in natural latex concentrate or natural latex compound, cost savings may be possible by optimizing chemical dispersion dosage, replacing existing highly foaming stabilizers and reducing lump waste with CHAINGUARD DB. When used in acrylonitrile butadiene rubber (NBR) latex compound, CHAINGUARD DB may partially or totally replace expensive and highly foaming sodium dodecylbenzene sulfonate (SDBS), offering cost savings with better latex compound stability, less foam and slower syneresis.

BACKGROUND

Although used as auxiliary additives with a low addition level, stabilizers can have dramatic impact on the overall stability of latex, as well as the properties, qualities and consistency of the manufactured dipped goods.

Natural latex concentrates have been produced and used for manufacturing dipped goods for over 100 years.^{1,2,3} To keep the natural latex concentrate from coagulating, an excessive amount of ammonia is added to preserve the latex and compensate for the evaporation loss during storage and transportation. Unfortunately, manufacturers who produce dipped goods using latex that contains ammonia commonly encounter problems associated with the high volatility of ammonia, such as pH drop, lump formation and surface skinning. In addition, ammonia has a very strong, pungent odor and is highly toxic to workers on the dipping line. Ammonia vapor also causes severe corrosion of steel equipment. To overcome the drawbacks of working with ammoniated latex, the natural latex industry has long sought safer chemistries that allow production of ammonia-free latex. At the 9th International Rubber Glove Conference and Exhibition 2018, ANGUS Chemical Company is introducing CHAINGUARD™ DB as a safe, low-odor and multifunctional chemistry for use in the production of ammonia-free, low-odor natural

latex concentrates. CHAINGUARD DB has been shown to improve stabilization of the latex compound at the dipping line, enhance pH stability, reduce lumping and discoloration of the latex and, when used in latex to make gloves, can improve thickness uniformity.

Synthetic latex such as NBR latex is protected by adsorbed emulsifiers. Additional stability is imparted by incorporation of carboxylic monomers such as acrylic acid or methacrylic acid. These neutralized surface-carboxylic groups provide negative charges for electrostatic stabilization. Having a surface rich with carboxylic groups provides excellent storage stability and mechanical stability as compared to natural latex with only surfactant stabilization.

In the glove dipping process, carboxylic groups from the latex react with coagulants such as $\text{Ca}(\text{NO}_3)_2$ through complexation. Then, a film of coagulated latex with porous structure filled with $\text{Ca}(\text{NO}_3)_2$ solution is formed on the glove former, a process typically known in the industry as gel setting. As the reaction between carboxylic group and $\text{Ca}(\text{NO}_3)_2$ proceeds, the film shrinks due to increased mechanical stress. The rate of film shrinkage is important; $\text{Ca}(\text{NO}_3)_2$ solution may be squeezed out from the gelled film if the gelation is too fast. Accumulated $\text{Ca}(\text{NO}_3)_2$ solution may drip from the former to the second latex dipping tank and cause lump formation. If gel setting is too fast and excessive syneresis is seen, SDBS may be added to slow down $\text{Ca}(\text{NO}_3)_2$ coagulation of latex. The sulfonate group has better tolerance to $\text{Ca}(\text{NO}_3)_2$ than a carboxylic group, allowing the use of SDBS for gel-setting control. However, the use of SDBS for gel-setting and syneresis control is not without problems. SDBS is highly foaming even under light mechanical agitation. When used in latex compounds, SDBS may introduce foaming that is suspected to cause pinholes in the dipped articles. As a result, there is continuous interest for cost effective low foam alternatives that perform similarly or better than SDBS in gel-setting and syneresis control.

EXPERIMENT

Preparation of ammonia-free latex concentrate and latex compound

Ammonia-free natural latex concentrate (CHAINGUARD DB-stabilized NRL) was prepared by dosing 1.2wt.% Chainguard DB into commercial high-ammonia latex concentrate (HA commercial NRL) and subsequently allowing ammonia to evaporate for 24 hours under ambient conditions with continuous stirring. pH and lump content were recorded before and after stirring both for both HA commercial NRL and CHAINGUARD DB-stabilized NRL.

Latex compounds were prepared according to table 1 formulations. Heat aging stability was conducted by aging at 60 °C and stirring latex compound at 500 rpm in a beaker. pH, viscosity change and lump formation were recorded.

Table 1, Prototype natural latex compound formulation

Material	Description	NH ₃	KOH	CHAINGUARD DB
60% Commercial HA NRL	NR Latex	166	-	-
60% Commercial HA NRL	NR Latex	-	166	-
60% NRL Stabilized with CHAINGUARD DB	NR Latex	-	-	166
50% Sulfur dispersion	Cross-linker	2	2	2
50% ZDEC dispersion	Accelerator	2	2	2
50% Zinc oxide dispersion	Activator	1.5	1.5	1.5
50% CaCO ₃ dispersion	Filler	2	2	2
KOH (10%)	pH adjustor	-	3	-

Method for rubber oxidation characterization

In a 50 mL plastic tube, a drop of ammonia or CHAINGUARD DB was added to 20 mL tap water, then a piece of Cu foil was placed in the tube above amine solution. Subsequently, 1 piece of natural rubber sheet is added to the tube. The color of the rubber sheet and copper foil was monitored over a period of 1 month.

Foam test

Foam test of CHAINGUARD DB or SDBS was done by shaking 20 mL of a 0.15% CHAINGUARD DB or SDBS solution in a 50 mL plastic tube for 1 minute. A picture of the solutions was taken after shaking to show the difference in foam levels between CHAINGUARD DB solution and SDBS solution.

The foam level of NBR latex was measured by shaking 20 mL NBR latex either without or with 0.3 phr CHAINGUARD DB or SDBS for 1 minute. A picture was taken to show the foam levels of each latex.

Surface tension measurement

Commercial natural latex concentrate or NBR latex were diluted with equal weight of water and dosed with 0.3 phr CHAINGUARD DB or SDBS and neutralized with KOH to pH=10. The latexes were kept at room temperature overnight prior to taking a surface tension measurement. Surface tension was measured using a Biolin Scientific surface tension analyzer by applying the Newton ring method.

Method for CaCl₂ stability test of NBR latex

CaCl₂ solutions with concentrations of 600 ppm, 700 ppm, 800 ppm, 900 ppm and 1000 ppm were prepared. Then 5 mL of CaCl₂ solution was poured into Petri dish. Subsequently, 0.3 g of latex neutralized with KOH to pH=10 and either stabilized with 0.3 phr CHAINGUARD DB or SDBS was added to the CaCl₂ solution and shaken well. The maximum concentration of CaCl₂ solution that didn't coagulate NBR latex was recognized as the CaCl₂ tolerance concentration.

Method for syneresis test

A 20% CaCl_2 solution in water was first prepared. Then a paper with size of 10 cm by 4 cm and thickness of $\sim 100 \mu\text{m}$ was dipped into the CaCl_2 solution for 20 seconds before being taken out for drying at 110°C for 5 minutes. Then, the dried CaCl_2 -impregnated paper was dipped into 20% TSC (total solid content) NBR latex (pH is neutralized to 10 by KOH) either stabilized with 0.3 phr CHAINGUARD DB or SDBS for 25 seconds. The film was then removed from the solution and the time taken for the first drop of water to drip from the dipped paper was recorded. The time taken for first drop of water drip was named “Syneresis Water Drop Time.”

RESULTS AND DISCUSSION

Figure 1 shows the pH of HA commercial latex and CHAINGUARD DB-stabilized ammonia-free latex both before and after stirring in a beaker for 24 hours. HA commercial latex concentrate shows abrupt pH drop to around 8, indicating that the majority of ammonia has evaporated away from the latex concentrate. On the contrary, CHAINGUARD DB-stabilized natural latex concentrate shows significantly better pH stability with only minor pH drop from initial of 9.7 to 9.3. The improved pH stability is due to the lower volatility of CHAINGUARD DB as compared to ammonia gas.

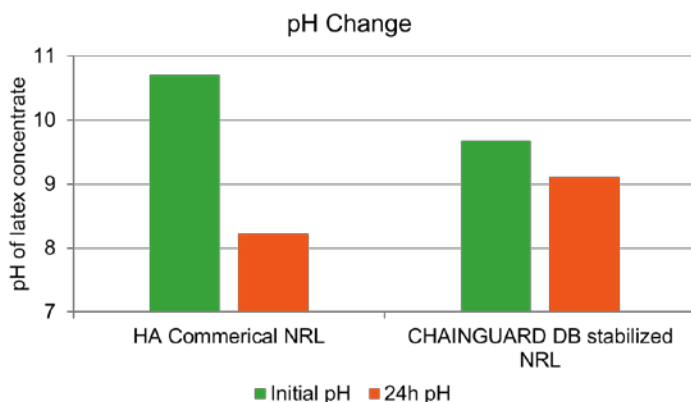


Figure 1 pH change of natural latex concentrate after stirring at 500 rpm for 24 hours.

After 24 hours of stirring, lumps from the latex concentrates were collected via filtration, dried and weighed. Figure 2 displays the percentage of lumps collected from HA commercial latex concentrate as compared to the CHAINGUARD DB-stabilized latex concentrate. The result clearly demonstrates improved stability of latex concentrates when CHAINGUARD DB was added as a stabilizer.

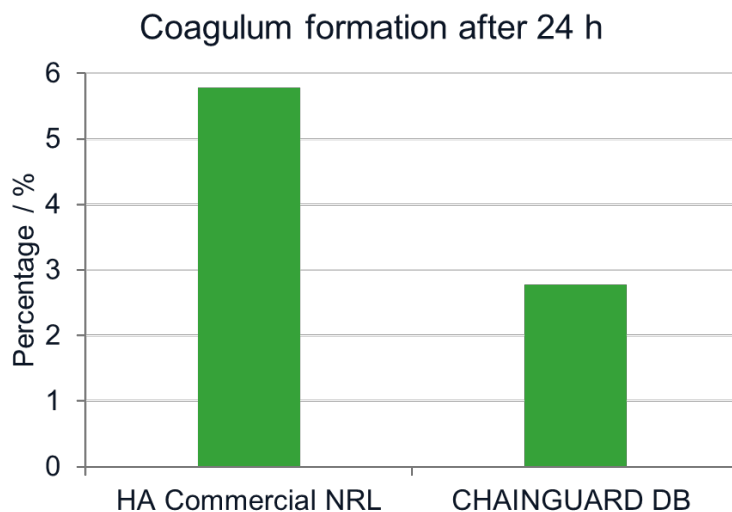


Figure 2 lump formation after stirring natural latex concentrate at 500 rpm for 24 hours

The latex concentrates were also compounded according to the formulations in Table 1. Figure 3 shows that the formulation with CHAINGUARD DB-stabilized natural-latex concentrate generated negligible lumping after heat aging test. On the contrary, formulations with commercial high-ammonia natural-latex concentrate generated substantially more lumps. In the absence of additional KOH as a pH stabilizer, the ammonia-based formulation displayed severe lump likely due to excessive loss of ammonia under the heat aging conditions and accelerated dissolution of ZnO and coagulation of latex by Zn^{2+} ions.

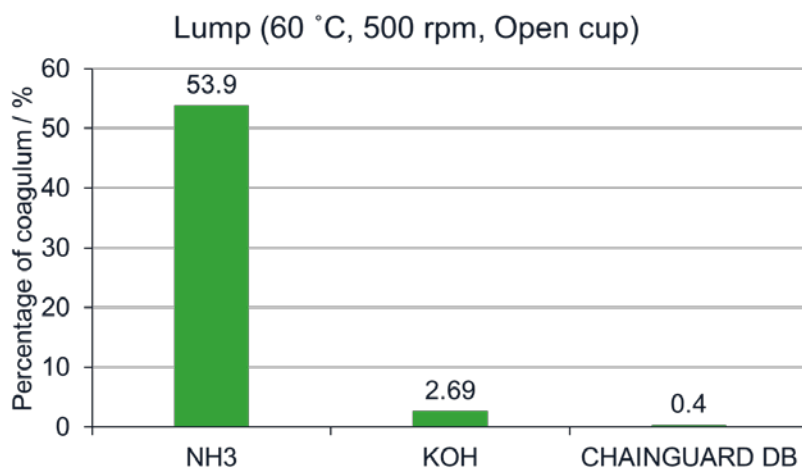


Figure 3 Lump formation after heat aging of natural latex compound at 60 °C at 500 rpm stirring for 1 hour.

ZnO is used as an activator to activate the sulfur crosslinking of natural rubber. It is typically added as particle dispersions to the latex compound. Once all ingredients are compounded into latex, a chemical aging process starts.⁴ As ammonia reacts with Zn^{2+} ions to form soluble Zn-Ammonia complex, ZnO particle is gradually etched and more Zn-ammonia complex are generated. These Zn-ammonia complexes react with surface adsorbed fatty acids from the latex and forms insoluble Zn-fatty acid soap. By charge

neutralization of the fatty acids with Zn-ammonia complex, natural latex particles are destabilized due to loss of electrostatic repulsion. Subsequently, latex particles aggregate with each other due to high hydrophobicity and coalesce into lump due to extremely low glass transition temperature.

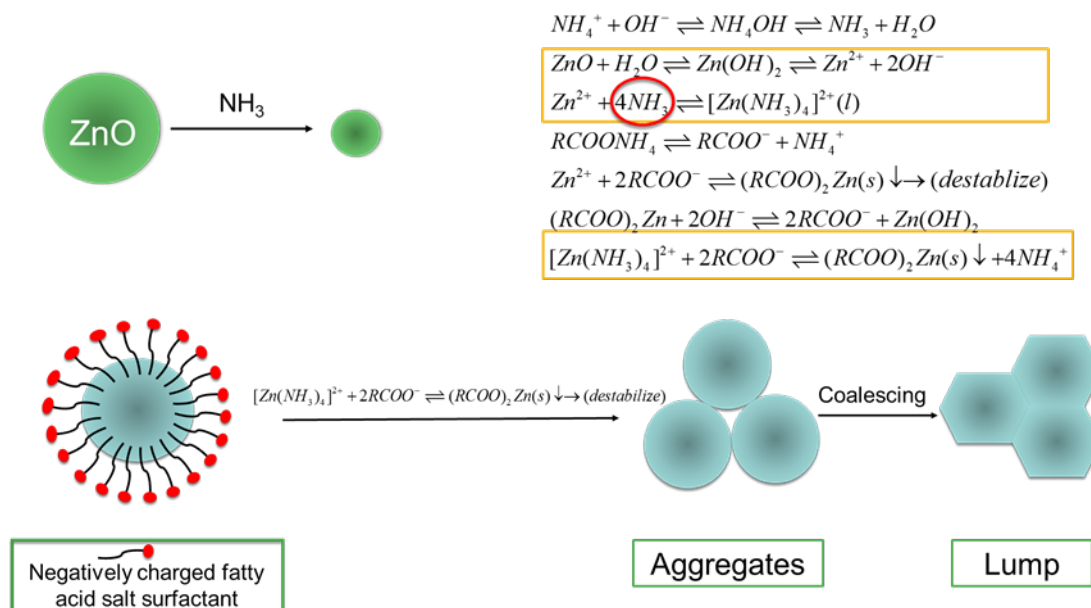


Figure 4 Proposed latex destabilization mechanism: Ammonia induced ZnO dissolution and latex coagulation

When CHAINGUARD DB is incorporated as stabilizer to natural latex compound, the active, 2-amino-2-methyl-1-propanol (AMP), forms an insoluble complex with ZnO. We postulate this insoluble Zn-AMP complex *in situ* coats the ZnO surface and prevents further etching of ZnO. The latex compound is left with limited amount of soluble Zn ion species to coagulate latexes. Therefore, latex compound stability is improved. By mixing ZnCl₂ with either ammonia solution or Chainguard DB, Figure 6 verified that the Zn-ammonia complex is soluble and Zn-AMP complex is insoluble as white precipitates.

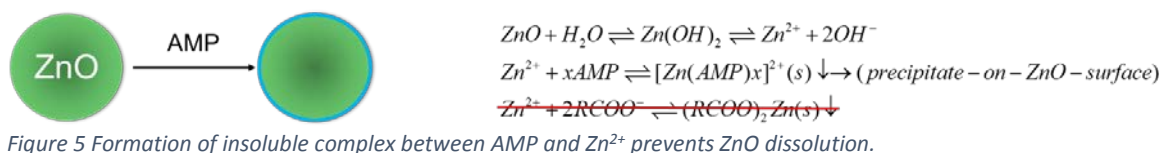


Figure 5 Formation of insoluble complex between AMP and Zn²⁺ prevents ZnO dissolution.

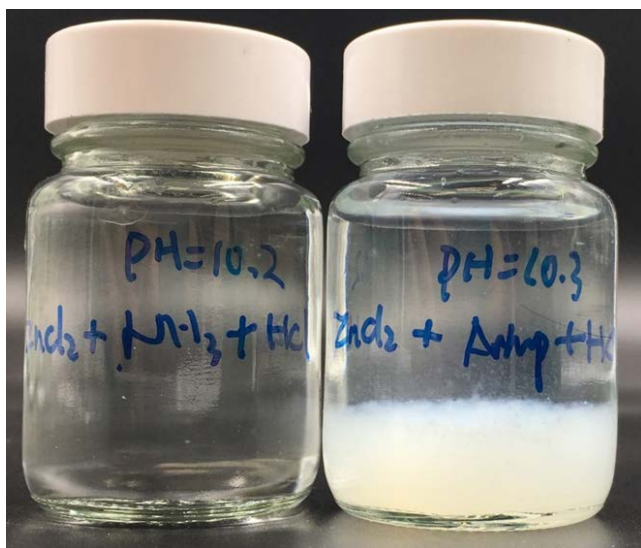


Figure 6 Image of Zn-Ammonia complex (left) and Zn-AMP complex (right).

CHAINGUARD DB may also be added as auxiliary stabilizer to existing formulations for enhancement of dipped film thickness uniformity. Result with addition of 0.25 phr as compound stabilizer in Table 2 shows drastically reduced thickness variation as compared to control sample.

Table 2 Glove finger to palm thickness variations.

	Control	0.25 phr Chainguard DB
Thickness variation (μm)	20	4

CHAINGUARD DB also demonstrated unexpected capability of inhibiting discoloration of natural latex concentrate as shown in Figure 7. When latex compound is stored under ambient conditions, headspace oxygen oxidizes natural rubber and causes formation of pinkish layer.⁵ This layer penetrates deeper into the latex compound with increasing of storage period. After 1 month of storage, latex compound with 2 phr CHAINGUARD DB shows the least discoloration as compared to formulations with ammonia or KOH as stabilizer.

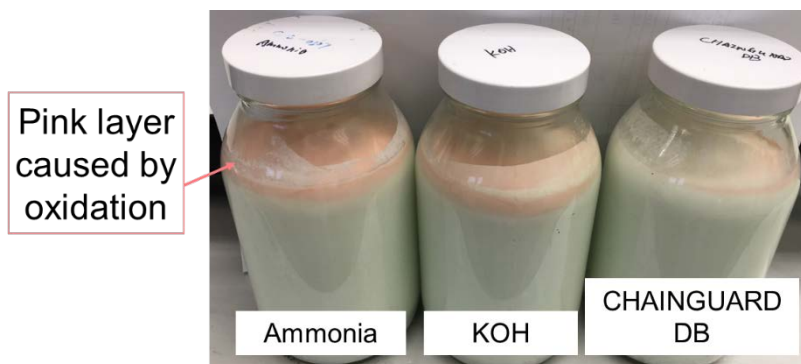


Figure 7 Oxidation of natural latex compound at the surface after exposure to head space air for 1 month. Incorporation of Chainguard DB to natural latex compound slows down oxidation induced pinkish layer formation.

The latex compounds were coagulated by natural drying and photos of the heat-aged (100 °C/1 week) dry rubbers were recorded as shown in Figure 10. The lighter color of dry rubber from CHAINGUARD DB-stabilized latex compound was observed as compared to dry rubber from ammoniated latex compound. The enhanced oxidation resistance of natural rubber could possibly imply improved heat-aging stability which may help extend shelf life of produced dipped goods such as gloves.

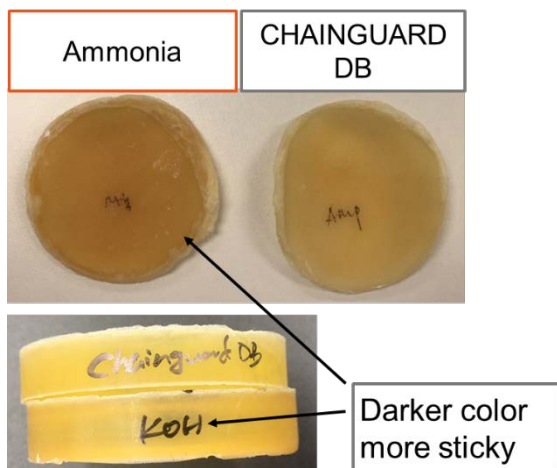


Figure 8 Color of natural rubber without and with Chainguard DB.

Various authors^{6,7,8} have identified Cu^{2+} ion as one of the key factors accelerating natural rubber degradation. Cu^{2+} is absorbed as trace metal nutrition by the natural rubber tree. Poulton et al⁸ has identified that ppm level of Cu^{2+} exists in produced natural latexes. This trace amount Cu^{2+} acts as strong catalyst to promote free radical generation on natural rubber polymer chain. Free radicals attack abstractable hydrogens from the polymer chain to cause polymer crosslinking or chain scissioning. Crosslinked natural rubber hardens or cracks. In the case of polymer scissioning, natural rubber becomes sticky due to reduced molecular weight. A change of color to pink or brown accompanies the oxidation process. CHAINGUARD DB is able to chelate with Cu^{2+} to form an inactive complex that minimizes catalytic activity that lead to rubber degradation. To demonstrate the copper ion accelerated degradation of the natural rubber, a proof of concept experiment was designed, as shown in Figure 9. A piece of natural rubber was soaked in

ammonia or CHAINGUARD DB containing water. A piece of copper was added to the solution as a source of copper ions. The mixtures were stored under ambient conditions for a month. Photos were taken to record the changes of rubber color and texture. Over the storage period, ammonia gradually etched the copper foil and formed soluble Cu-ammonia complex. The dissolved Cu-ammonia complex catalyzed rubber degradation and the color of rubber sheet changed to pink after storage for only 1 week. The rubber sheet was completely rotten with negligible mechanical strength and elasticity. On the contrary, the rubber sample soaked in the CHAINGUARD DB sample did not show any change of color or mechanical strength even after 1 month of storage.

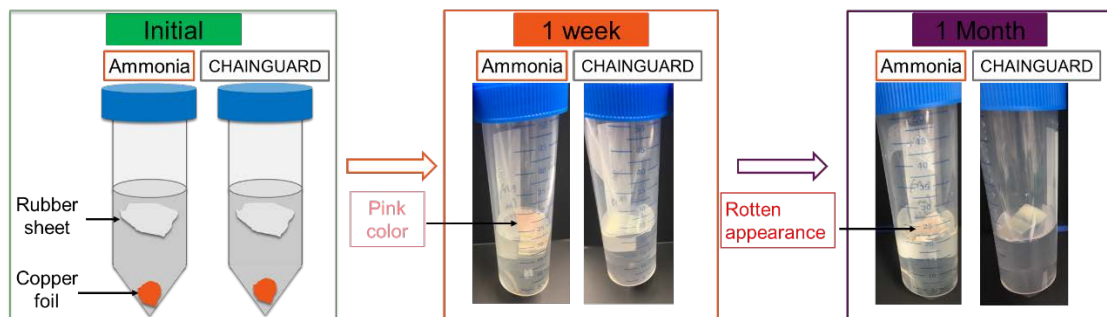


Figure 9 Color change of natural rubber sheets exposed to copper ion solution. Catalysed rubber degradation was observed in ammoniated water with copper foil.

As an organic amine, CHAINGUARD DB is able to neutralize fatty acids to form a fatty acid amine salt surfactant. Due to the larger size of the active AMP molecule compared to Na^+ , K^+ or NH_4^+ ion, the fatty acid-AMP salt tends to pack looser at water/air interface compared to caustic-neutralized fatty acids. The loose packing results in a weaker hydrophobic attraction force between adjacent surfactant molecules, therefore a lower surface tension is achieved as compared to caustic-neutralized fatty acid surfactant. An illustration depicting the anticipated packing schemes of neutralized surfactants at water/air interface is shown in figure 10. Figure 11 shows dosing 0.3 phr to CHAINGUARD DB to medium ammonia natural latex concentrate slightly reduced surface tension from 35.15 mN/cm to 34.85 mN/cm.

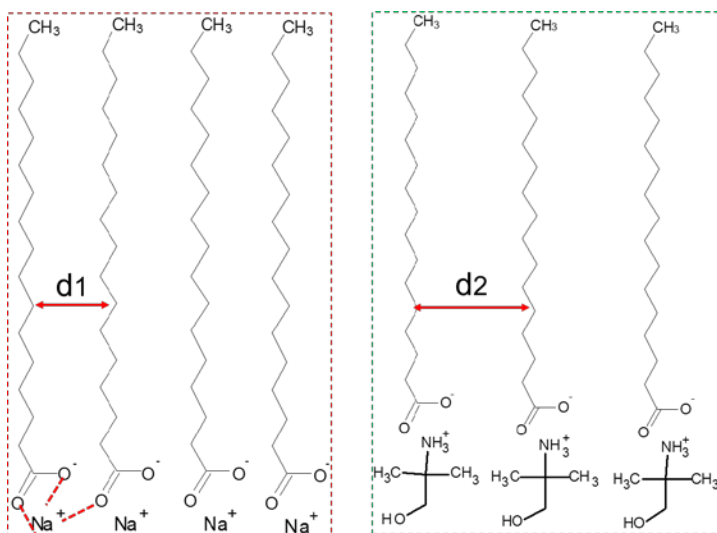


Figure 10 Proposed surfactant packing at water-air interface with CHAINGUARD DB-neutralized fatty acids compared to NaOH-neutralized fatty acids.

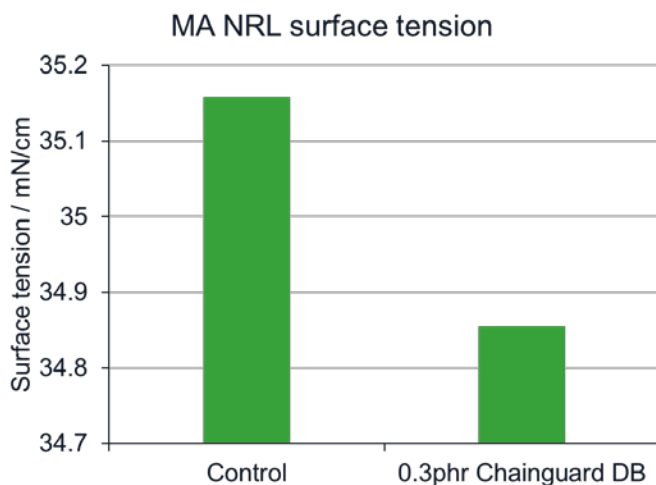


Figure 10 Surface tension of medium ammonia natural latex concentrate dosed without (control) and with 0.3 phr of CHAINGUARD DB.

In NBR glove manufacturing processes, SDBS is widely used as a compound stabilizer to improve compound stability and reduce syneresis. However, as a sulfonate surfactant, SDBS tends to generate a very stable and large volume of foam upon agitation. Figure 12 shows foam of 0.15% CHAINGUARD DB and 0.15% SDBS solutions. CHAINGUARD DB generated negligible foam after shaking for 1 minute. Whereas SDBS generated large

volume of foam that totally filled the plastic tube. Even after 30 minutes of static resting, the foam in SDBS solution remained stable.



Figure 12 Foam generated by shaking 0.15% solutions of Chainguard DB and SDBS.

Latex with lower surface tension tends to spread on the polar former surface better, which may, in turn, enhance wetting and reduce pinhole formation. When incorporated into selected NBR latex as shown in Figure 13, CHAINGUARD DB reduced the surface tension to the same level as with SDBS. However, foam generated by shaking of latex was much less for latex stabilized with CHAINGUARD DB than with SDBS (Figure 14). The reduced latex surface tension and lower foaming with CHAINGUARD DB indicates more favorable dipping properties such as less pinhole and better compound stability, as compared with SDBS.

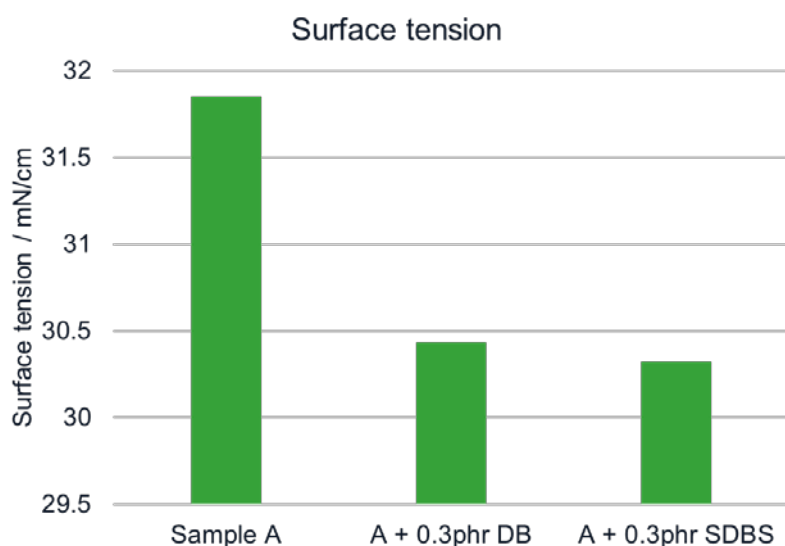


Figure 13 Surface tension of NBR latex sample A, sample A with 0.3 phr CHAINGUARD DB and sample A with 0.3 phr SDBS. All latexes were neutralized with KOH to pH=10.

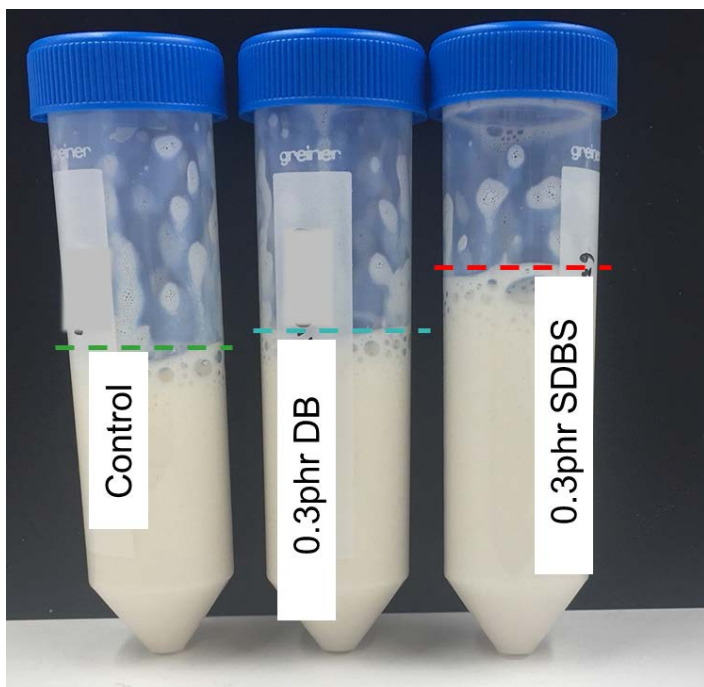


Figure 14 Foam generated after shaking of commercial NBR latex(Control), commercial NBR latex with 0.3 phr CHAINGUARD DB and commercial NBR latex with 0.3 phr. All latexes were neutralized with KOH to pH=10.

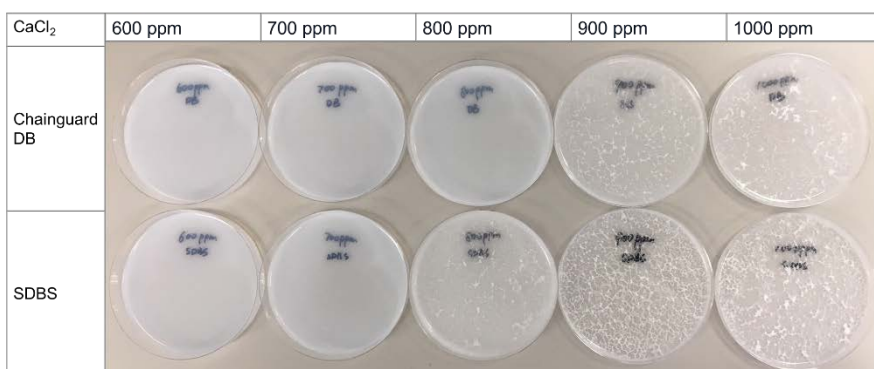


Figure 14 Comparison of CaCl₂ stability of 0.3 phr CHAINGUARD DB and SDBS stabilized NBR latex samples. Both latexes were neutralized with KOH to pH=10

The stability of latexes was tested against different concentrations of CaCl₂ solution. The minimum concentration of CaCl₂ that induced coagulation of NBR latex was determined by mixing stabilized latex with CaCl₂ solution. Figure 14 shows the minimum CaCl₂ concentration for coagulation of CHAINGUARD DB stabilized NBR latex is 900 ppm. For SDBS stabilized NBR latex, the minimum CaCl₂ coagulation concentration is 800 ppm. The results demonstrate improved NBR latex stability with CHAINGUARD DB than with SDBS as a stabilizer.

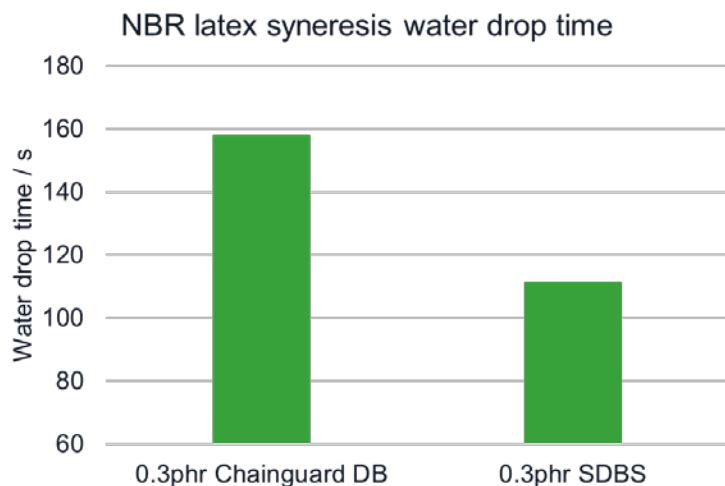


Figure 15 Syneresis water drop time comparison of NBR latex stabilized with CHAINGUARD DB or SDBS. Both latexes were neutralized with KOH to pH=10.

Syneresis water drop time was adopted to characterize the speed of gelation after latex dipping. Fast gelation results in quick shrinking of gelled film with CaCl_2 coagulant solution being squeezed out faster. Time taken for the first drop of CaCl_2 solution dripping from the dipped film was recorded as shown in Figure 15. Syneresis water drop time is significantly longer for NBR latex stabilized with 0.3 phr CHAINGUARD DB than with 0.3 phr SDBS, indicating improved syneresis control with CHAINGUARD DB than with SDBS.

When syneresis was tested on a NBR latex neutralized with only CHAINGUARD DB (10 phr) or only KOH (2 phr), formulation with CHAINGUARD DB-neutralized NBR showed no sign of syneresis even after 500 seconds, formulation with KOH-neutralized NBR latex showed syneresis water drop after 130 seconds (Figure 16). The extent of syneresis improvement with CHAINGUARD DB as a stabilizer may vary from different sources of NBR latex. Generally, increasing dosage of CHAINGUARD DB will increase the syneresis water drop time.

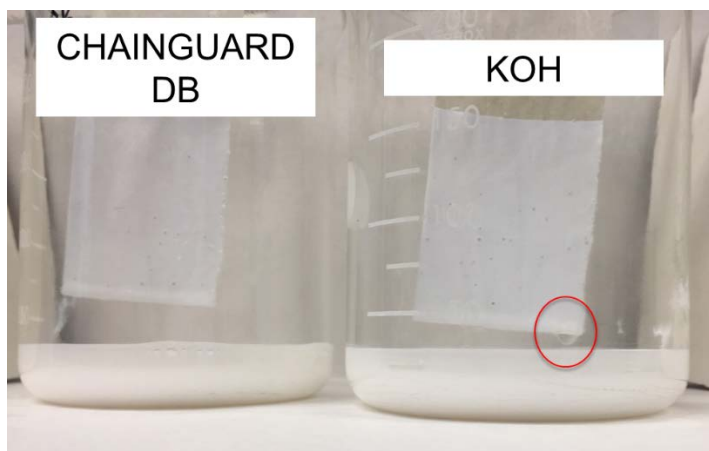


Figure 11 Comparison of syneresis water drop time of NBR latex neutralized with CHAINGUARD DB or neutralized with KOH.

CONCLUSIONS

With incorporation of a suitable stabilizer such as CHAINGUARD DB, ammonia-free low-odor natural latex concentrate may be produced with improved pH stability, viscosity stability and reduced lumping. When added as an auxiliary stabilizer to natural latex compound, CHAINGUARD DB can enhance compound stability, and improve heat aging and dipped-film thickness uniformity. As a low-foam, low-cost, better performing alternative to SDBS, CHAINGUARD DB helps improve the chemical stability of NBR latex compound while reducing foam and syneresis issues compared to SDBS.

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