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The Effect of Hydrophobically Modified Inulin on the Properties of Natural Rubber Latex Concentrates

MANROSHAN, S.*#, AMIR-HASHIM M.Y.* AND BOOTEN, K.**

Natural rubber (NR) latex is a dispersion of rubber particles in an aqueous phase. By virtue of the naturally occurring surface active materials surrounding each particle, the rubber particles are therefore prevented from coalescing together. However, microbe activities in non-preserved latex may destroy the surface active properties of these natural materials. Hence, NR latex is typically preserved with ammonia to maintain its alkalinity of pH 10 and above. In this study, a biobased surfactant was added to the deammoniated natural rubber latex concentrate to enhance the stability of the latex. The hydrophobically modified polyfructose (Inutec® SP1), thought to be similar to some of the naturally occurring surfactants on the rubber was incorporated into the latex at different ratios and its effect on some of the important properties of the latex were investigated. The addition of 0.25 p.h.r. of the surfactant increased the mechanical stability time (MST) of the latex concentrates by 500 s. Up to six weeks of storage, not much change was observed in the viscosity although the volatile fatty acid number (VFA No.) of the concentrates increased slightly. However, as the pH reduced further below 10, the effectiveness of the surfactant decreased. The MST reduced whereas the VFA No. and viscosity of the latex concentrates increased.

Key words: natural rubber; inulin; surfactant; mechanical stability; volatile fatty acids

The preservation of natural rubber (NR) latex is an important aspect for high-quality latex in the product manufacturing sector. The bacterial activities occurring in unpreserved NR are known to yield acidic substances. These acidic substances generally cause spontaneous coagulation of latex, subsequently affecting the quality of latex. From the dawn of the industry, ammonia has been a favoured latex preservative. Among the advantages of ammonia are that it is inexpensive as well as easy to use and remove. On the other hand, its disadvantages include its pungent odour, side reaction with some chemicals and changes occurring over time. Many other preservation systems have been tried, but none has found its way over ammonia in industrial applications. Preservation of NR latex is mainly to reduce bacterial activity, while maintaining the latex quality.

Surface active agents, commonly known as surfactants are compounds which bring about marked modifications to the surface properties of liquid media. They are added to latex to enhance its stability during the latex stage. These compounds are very important for technological applications[1], particularly in the field of textiles, paper, printing inks, coatings, adhesives and paints. In recent years,

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*Rubber Research Institute of Malaysia, Malaysian Rubber Board, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia
**ORAFTI NON-FOOD, Aandorenstraat 1, B-3300 Tienen, Belgium
#Corresponding author: (e-mail: manroshan@lgm.gov.my)

the use of polymeric surfactants as dispersants for solids in liquids and as emulsifiers[2] has gained much attention. Initially, the common polymeric surfactants are based on synthetic chains namely, polystyrene chains or poly(ethylene oxide) chains[3]. In this view, surfactants based on polysaccharide chains are the current focus as they are biodegradable and renewable[4]. In this paper, the usage of such a surfactant is extended to NR latex. We report the use of hydrophobized inulin (polyfructose) in deammoniated NR latex concentrate. The effect of the surfactant on the mechanical stability time (MST), volatile fatty acid (VFA), viscosity, alkalinity and pH are investigated.

MATERIALS AND METHODS

Materials

High ammoniated (HA) latex concentrate was purchased from Lee Latex Sdn. Bhd., Malaysia whereas the surfactant, Inutec® SP1 was supplied by Orafti Bio Based Chemicals, Belgium. Inutec® SP1 is a non-ionic, polymeric surfactant based on inulin (polyfructose) that has been hydrophobically modified by introducing several alkyl groups on the linear polyfructose chain. The structure and properties of the polymeric surfactant has been described elsewhere[5,6] while the composition and specification of Inutec® SP1 is as shown in *Table 1*.

Methods

Sample preparation. The HA latex concentrate was initially aerated for 2 hours to reduce its ammonia content (DA latex). Due to the low solubilizing property of Inutec® SP1, the surfactant was dispersed to 10% (w/w) using distilled water. The surfactant was then added to the latex according to the formulations in *Table 2* and the latex was incubated with the surfactant for one week at room temperature.

MST, VFA No., alkalinity, viscosity and pH of the latex concentrates were measured on the second week of storage. All tests were repeated again every two weeks for a total of 16 weeks.

Mechanical stability time (MST). The MST was measured with reference to the *ISO 35:1989(E)*[7] test method. A Klaxon Mechanical Stability Tester was used for this purpose. The end point was taken within seconds at the first appearance of flocculum. The appearance of flocculum was determined by spreading a drop of the test sample on the palm of the hand.

Volatile Fatty Acid Number (VFA No.). The VFA No. was determined according to the *ISO 506:1992(E)*[8] test method. The test was carried out in duplicates and the VFA No. was calculated using *Equation 1* below:

$$VFA\ No. = \left[\frac{134.64cV}{mTSC}\right] \times \left[50 + \frac{m(100-DRC)}{100\,\rho}\right] \quad \ldots\ 1$$

where

m is the mass of sample (grams);
c is the actual concentration of barium hydroxide solution (0.005 mol/dm^3);
v is the volume of barium hydroxide solution used (ml);
ρ is the density of the serum (1.02 mg/m^3)

Viscosity. The viscosity was measured using a Brookfield Viscometer Model LVT with reference to the *ISO 1652 – 1985(E)*[9] test method. An average of two duplicates was used as the viscosity of the latex.

Alkalinity. The alkalinity was measured with reference to the *ISO 125:1990(E)*[10] test method. Sulphuric acid 0.05M was added to the latex concentrate until its pH was reduced

TABLE 1. COMPOSITION AND SPECIFICATION OF THE SURFACTANT

Chemical description	Hydrophobized inulin
Composition specification	
Active substance (%)	Min 95.0
pH (20ºC)	5.0 – 8.0 (1% w/v solution in water)
Product information	
Appearance	Fine, off – white powder
Mean molar mass (g/mol)	> 4500
Melting point	170ºC
Tapped density (kg/l)	± 0.3
Water solubility	Low; ± 4% max
Dispensability in water	Good – requires stirring

TABLE 2. FORMULATIONS FOR LATEX CONCENTRATES WITH DIFFERENT AMOUNTS OF SURFACTANT

	Dry weight (p.h.r.)						
Formulations	A	B	C	D	E	F	G
HA Latex	100	100	–	–	–	–	–
Deammoniated Latex	–	–	100	100	100	100	100
Inutec® SP1	0	0.5	0	0.25	0.5	0.75	1.0

to a value of 6 ± 0.5. The alkalinity was then calculated using *Equation 2* below:

$$Alkalinity = \frac{3.4 \times 0.05 \times V}{m} \qquad \ldots 2$$

where

V is the volume of acid used (ml);

m is the mass of sample (grams)

pH. The pH of the latex was measured using a Hanna pH meter model pH 211 equipped with the M 411087 electrode. The electrode was inserted into a beaker containing 200 ml of latex concentrate and the pH was recorded once the reading of the pH meter stabilized.

RESULTS AND DISCUSSION

The stability of NR latex is normally gauged by the emergence of rubber flocs in the latex over time. The emergence of these flocs is hastened, thus the mechanical stability time of the latex can be estimated. *Figure 1* shows the effect of the surfactant on the mechanical stability of various formulated latex concentrates after a storage period of two weeks. It is obvious from the MST results that deammoniation reduced the mechanical stability time of NR latex from 1700 ± 300 seconds for HA latex to 1300 ± 300 seconds for DA latex.

With the addition of 1.0 p.h.r. bio-based surfactant, the latex stability of DA latex concentrate increased drastically to more than 3600 seconds which is almost twice the stability time of normal latex concentrate. It is worth noting that this reading approaches the limit of the MST tester used in this study.

The MST of DA latex concentrates was monitored for a period of 16 weeks and as illustrated in *Figure 2*, the stability of the latex concentrates clearly improved with the addition of the surfactant compared to the mixture without surfactant. The apparent addition of 0.25 p.h.r. surfactant increased the MST by 500 seconds. The improvement in the stability of these latex concentrates can be related to the structure of the biobased surfactant (Inutec® SP1)[6] where, several alkyl groups attached to the linear polyfructose chain, may anchor onto the rubber particles leaving the loops of polyfructose dangling in the solution and therefore providing enhanced steric stabilization to the latex[11,12].

The MST values of the latex mixture with low levels of surfactant (0.25 p.h.r.) were consistent throughout the 16 week period, while the latex concentrates with higher levels of surfactant showed a trend of decreasing MST with time. It is thought that this phenomenon may be associated with the interaction between the polyfructose loops and other non-rubbers present in the latex similar to the reactions involving polysaccharides generating heterocyclic compounds that still possess glycosidic substituents. The increasing amount of these compounds with storage time may affect the stability time, and this explains the decrease in MST with storage time. Despite this decrease, the MST of these latex concentrates were still relatively longer than that of the latex concentrates with no surfactant.

Figure 3 shows the comparative plots of mechanical stability time between HA and DA latex concentrates with and without surfactant. Compared to the DA latex concentrate, HA latex concentrate with surfactant gave a higher level of stability. Together with ammonia, the surfactant improved the stability of the latex but as described earlier, the effectiveness of the surfactant decreased with time. Therefore, the elevated MST of the latex with surfactant approached its normal MST after 16 weeks.

Another important parameter to gauge the stability of latex is the level of volatile fatty acids produced during storage. *Figures 4* and *5* summarize the relationship between the added surfactant and volatile fatty acids present in the HA and DA latex concentrates.

From *Figure 4*, it is observed that the volatile fatty acid number (VFA No.) increased gradually with storage time reaching a value of 0.10 on the sixteenth week. A slight change was observed in the VFA No. of latex with 0.5 p.h.r. of surfactant. In DA latex (*Figure 5*), the increase in VFA No. for the latex with and without surfactant was much faster compared to the HA latex concentrates.

In natural rubber latex, the volatile fatty acids are formed by the metabolism of indigenous latex carbohydrates by micro-organisms. The addition of ammonia as a preservative reduces the microorganism activity, therefore reducing the formation of volatile fatty acids. Even so, the volatile fatty acids do increase with storage time as evident in *Figure 4*. The addition of the slighty acidic surfactant did not affect the VFA formation in HA latex concentrates. However, in the already deammoniated concen-trates (DA latex), the addition of surfactant further reduced the ammonia content. As a result, the formation of VFAs increased as a result of the rise in bacterial activity.

Figures 6 and *7* show the effect of the surfactant on the viscosity of HA and DA latex concentrates. The results show very little difference in the viscosity of the concentrates up to six weeks of storage. However, the viscosity of the concentrates with surfactant increased rapidly after six weeks with a prominent increase observed in the HA latex concentrate (*Figure 6*).

The rise in viscosity on storage is probably due to the chain density[13] of the surfactant. As the chain density increased with addition of

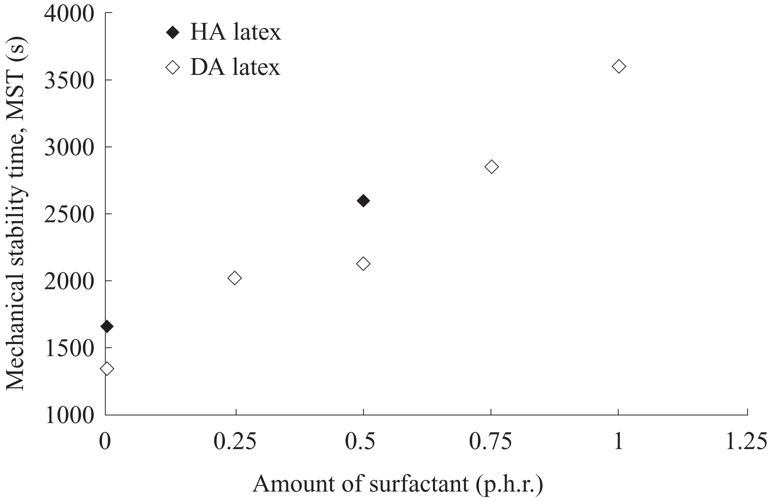

Figure 1. Effect of surfactant on the mechanical stability time of HA and DA latex concentrates on the second week of storage.

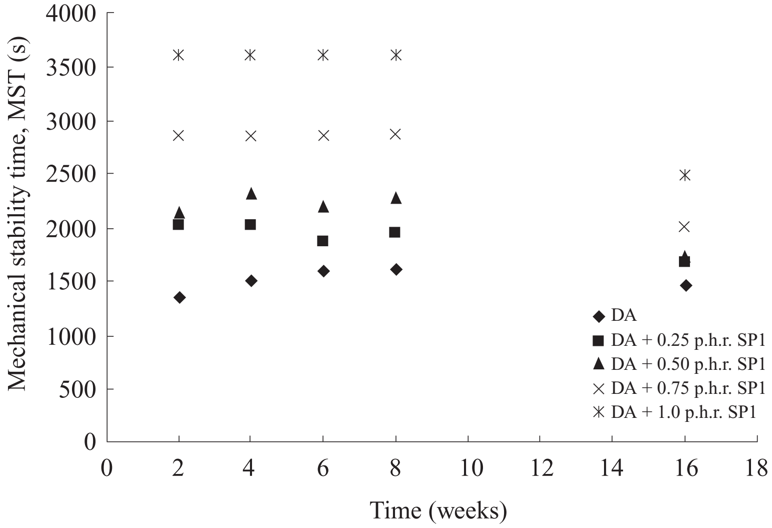

Figure 2. Effect of surfactant on the mechanical stability time of DA latex concentrates.

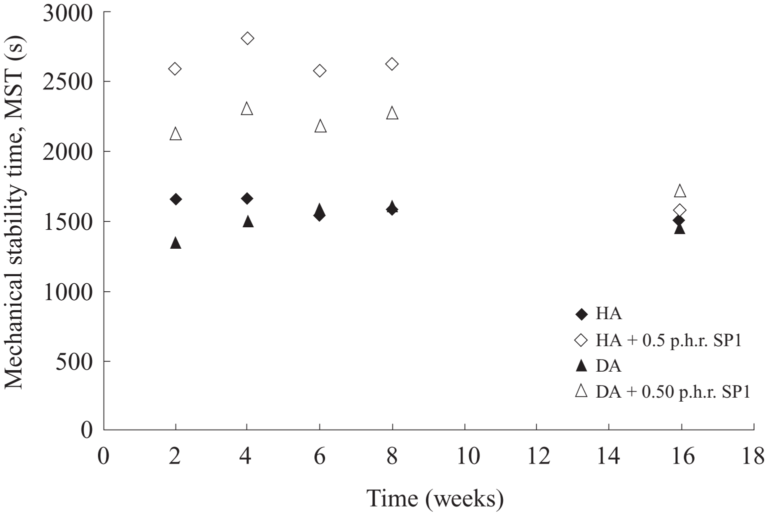

Figure 3. Comparison of the mechanical stability time between HA and DA latex concentrates with and without surfactant.

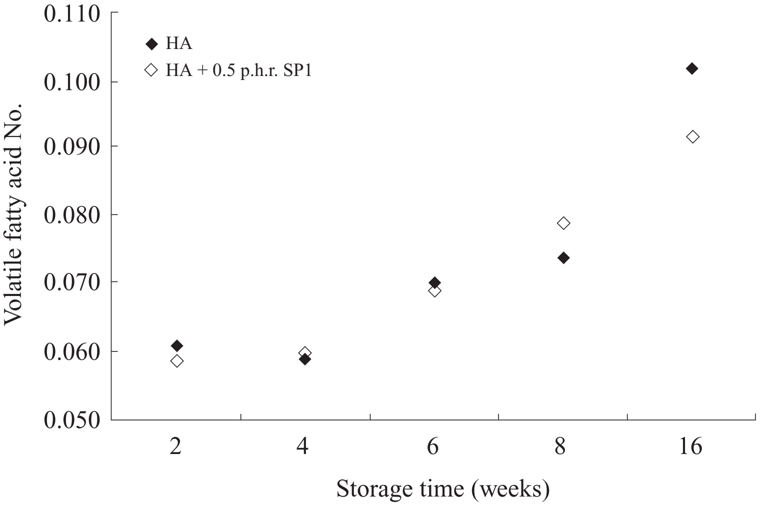

Figure 4. The effect of surfactant on the volatile fatty acid no. of HA latex concentrates.

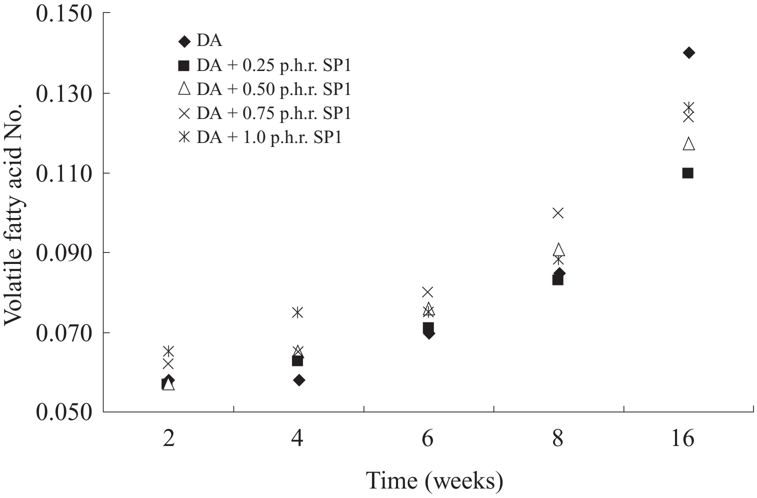

Figure 5. The effect of surfactant on the volatile fatty acid no. of DA latex concentrates.

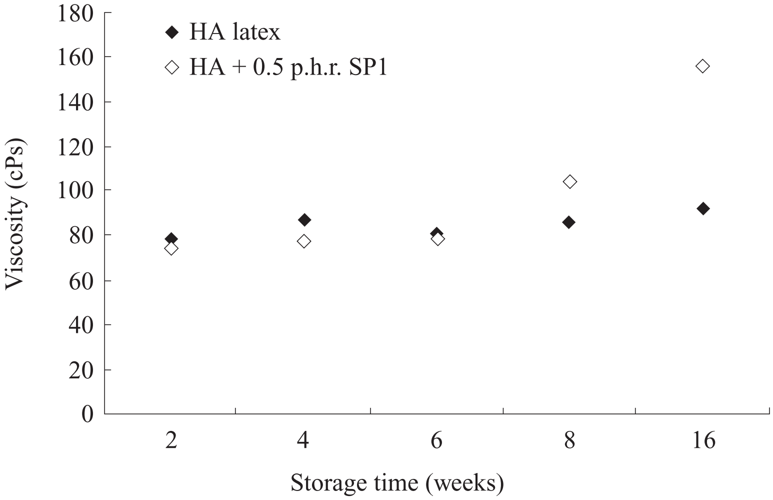

Figure 6. The effect of surfactant on the viscosity of HA latex concentrates.

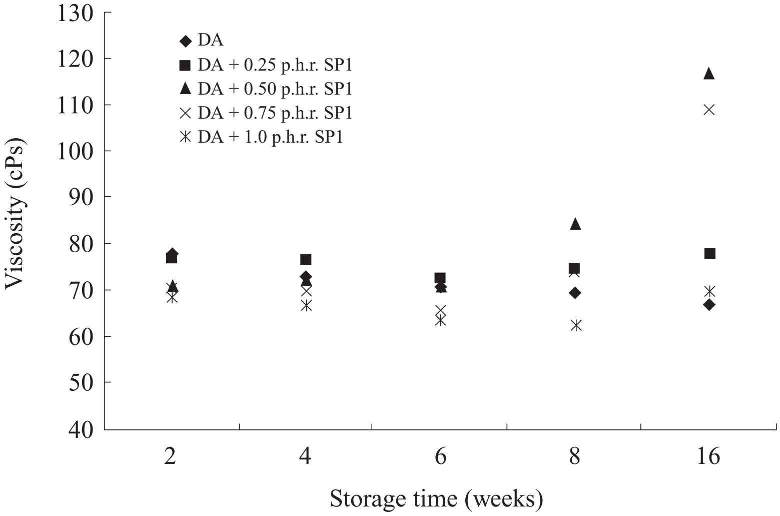

Figure 7. The effect of surfactant on the viscosity of DA latex concentrates.

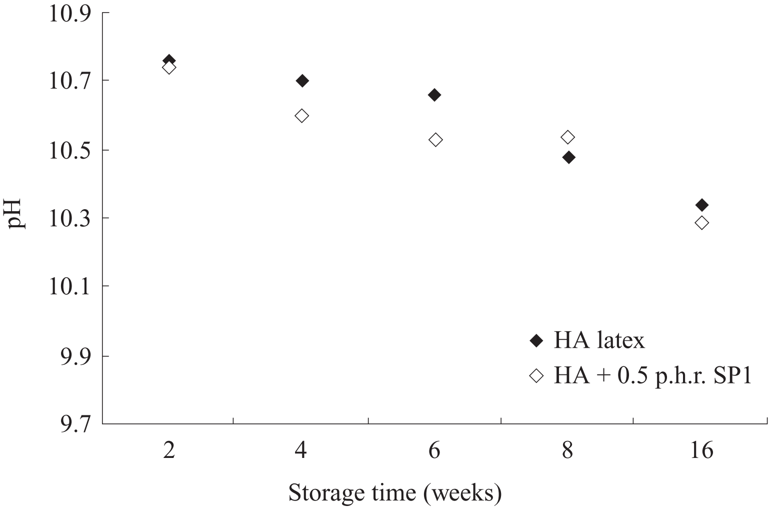

Figure 8. Effect of surfactant on the pH of HA latex concentrates.

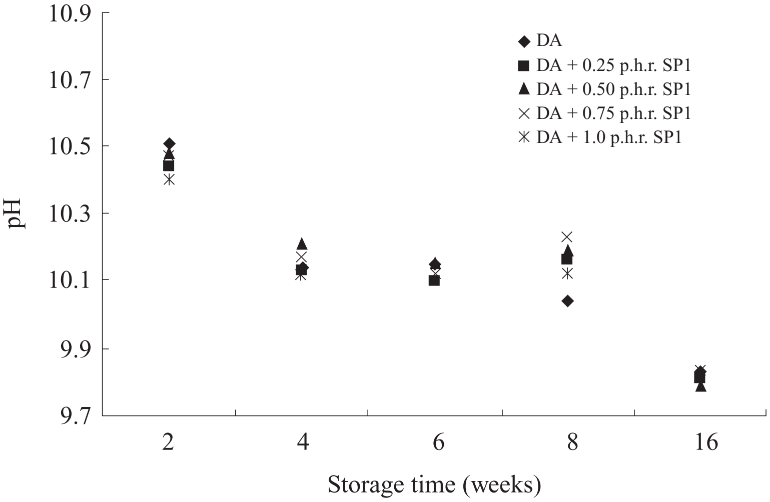

Figure 9. Effect of surfactant on the pH of DA latex concentrates.

surfactant (0.5 p.h.r. and 0.75 p.h.r.), a higher degree of chain entanglement occurred, which led to the rise in viscosity. However, when more surfactant was added (1.0 p.h.r.) into the latex, the viscosity of the concentrate did not increase much. It is possible that when the surfactant concentration reaches a certain amount, the polymer tends to coil into a more compact conformation, leading to a reduction in the final viscosity[14].

The stability of NR latex depends very much on its alkalinity and generally, high alkalinity is preferred for NR latex. Alkalinity in NR latex is defined as the amount of free ammonia available in the latex. In this study, minute changes were observed in the alkalinity of the latex concentrates except for a slight reduction of 0.1% ammonia content which could be due to the removal of ammonia during sampling.

However, a significant change in the pH of the concentrates was observed throughout the study. The reduction of pH in HA and DA latex concentrates with and without surfactant was about 0.4 and 0.8 pH units, respectively. Though a trend of gradual pH reduction was observed for HA latex concentrates, the trend observed for DA latex concentrates showed otherwise. For DA latex concentrates (*Figure 9*), a sharp reduction in pH from 10.4 on the second week to 10.1 on the fourth week was observed. After that, the pH remained stable until the sixth week and then reduced further until it reached 9.8 on the sixteenth week.

From the results of *Figures 8* and *9*, it is probable that the surfactant functioned well when the pH of the latex concentrates was above 10. Subsequently, below a pH of 10, the effectiveness of the surfactant reduced. This would then explain the reduction in the MST and the increase in the VFA No. as well as the viscosity of the latex concentrates above six weeks of storage time.

CONCLUSION

It was evident that the biobased surfactant had an effect on the properties of natural rubber latex concentrates. As a result of the surfactant, the mechanical stability time increased 500 s for every addition of 0.25 p.h.r. surfactant. Up to six weeks of storage, only minute changes were observed in the viscosity although the VFA No. increased slightly. However, as the pH reduced further below 10, the effectiveness of the surfactant decreased. The MST reduced while the VFA No. and the viscosity of the latex concentrates increased.

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REFERENCES

1. PARFITT, G.D. (1973) *Dispersions of Powders in Liquids. 2nd edition.* London: Applied Science Publishers Ltd.

2. TADROS, TH. F. (1999) Polymeric Surfactants: Stabilization of Emulsions and Dispersions. *In Principals of Polymer Science and Technology in Cosmetics and Personal Care*. (*Goddard, E.D., Gruber, J.V., eds.*) New York: Marcel Dekker.

3. PIRMA, I. (1982) *Polymeric Surfactants*. New York: Marcel Dekker.

4. MENGER, F.M., MBADUNGHA, B. N. A. (2006) Gemini Surfactants with a Disaccharide Spacer. *J. Am. Chem. Soc*. **123**, 875.

5. TADROS, TH. F., VANDAMME, A., LEVECKE, B., BOOTEN, K. AND STEVENS, C.V. (2004) Stabilization of Emulsions using Polymeric Surfactants based on Inulin. *Adv. Colloid Interface Sci*. **207**, 108–109.

6. TADROS, TH. F., VANDAMME, A., LEVECKE, B., BOOTEN, K. AND STEVENS, C.V. (2005) Stabilisation of Emulsions using Hydrophobically Modified Inulin (Polyfructose). *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **250**, 133.

7. INTERNATIONAL ORGANIZATION FOR STANDARDIZATION (1989) Natural Rubber Latex Concentrate – Determination of Mechanical Stability. *ISO 35:1989(E)*.

8. INTERNATIONAL ORGANIZATION FOR STANDARDIZATION (1992) Rubber Latex, Natural, Concentrate – Determination of Volatile Fatty Acid Number. *ISO 506:1992(E)*.

9. INTERNATIONAL ORGANIZATION FOR STANDARDIZATION (1985) Rubber Latex – Determination of Viscosity. *ISO 1652 – 1985(E)*.

10. INTERNATIONAL ORGANIZATION FOR STANDARDIZATION (1990) Natural Rubber Latex Concentrate – Determination of Alkalinity. *ISO 125:1990(E)*.

11. BLACKLEY, D.C. (1997) *Polymer Latices. Science and Technology,* **2**, 106.

12. NORMA, A.M.M. AND LOPEZ, M.G. (2002) Generation of Maillard Compounds from Inulin during the Thermal Processing of Agave Tequilana Weber Var. azul. *J. Agric. Food Chem*., **50**, 806.

13. SPRONG, E., DE WET – ROOS, D., TONGE, M AND SANDERSON, R. (2004) Solution and Latex Properties of Model Alkali-Soluble Rheology Modifiers, Synthesized *via* the Reversible Addition-Fragmentation Chain Transfer Process, and the Effects of the Ethylene Oxide Chain Length on the Rheological Properties. *J. Poly. Sci. Part B: Polym. Phys*., **42(13)**, 2502–2512.

14. TAM, K. C., FARMER, M. L., JENKINS, R. D., BASSETT, D. R. (1998) Rheological Properties of Hydrophobically Modified Alkali-soluble Polymers: Effects of Ethylene-oxide Chain Length. *J. Poly. Sci. Part B: Polym. Phys*., **36**, 2275–2290.