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Full Paper

Investigation of Field Performance and Film Properties of Natural Rubber Latex Preserved with a Novel Chemical

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Abstract

The traditional long-term preservative system of latex has an impact on environmental air pollution by ammonia and leads to the production of carcinogenic nitrosamine substances by tetramethyl thiuram disulfide (TMTD). In this research, ammonia and a novel preservative with polysulfidic link were compounded and tested as a novel traditional long-term latex preservative system, to overcome the drawbacks of traditional preservative systems. Control samples were prepared with ammonia as the standard preservative. In addition, ammonia and the novel chemical mixed samples were also prepared for investigating the combined effect. After the preservation treatment, the stable nature of field NR latex was evaluated via the Volatile Fatty Acid (VFA) test based on ASTM D 1076 standard. The Dry Rubber Content (DRC) test and Total Solid Content (TSC) test were carried out for VFA calculation purposes based on ISO126:2005 and ASTM D 1076 standards, respectively. The alkalinity test was carried out to maintain the required ammonia content in latex. In the first trial, traditional dispersion preparation of novel chemical dispersion failed due to the large particle size of the novel chemical. Therefore, two different novel chemical dispersions were prepared in the second trial, where dispersions 1 and 2 were prepared with wetting agents and without using a wetting agent, respectively. It was found that 0.020%v/v and 0.025% v/v concentrations of the novel chemical from dispersion 1 allowed the preservation of field NR latex for 8 days. A low concentration (0.015% v/v) of the novel chemical was able to keep latex with good stability for 5 days. The novel chemical dispersion without a wetting agent exhibited a marvelous preservative system to NR latex than with a wetting agent, because the wetting agent creates a barrier between particles of novel chemical and latex particles. The novel preservative acts as a good preservative while reducing the fumes of ammonia being emitted and eliminating the carcinogenic nitrosamine emission from TMTD.

Keywords: Natural rubber, latex preservatives, novel preservative, tetramethyl thiuram disulfide (TMTD)

Introduction

Natural rubber (NR) latex is a white sap and stable dispersion of cis-1,4- polyisoprene in an aqueous phase that exuded from the *Hevea brasiliensis* tree. NR latex has three basic phases upon centrifugation as rubber particles phase, lucid phase, and aqueous non-rubber phase. Where, the aqueous phase contains proteins, carbohydrates, amino acids, enzymes, and other serum constituents [1]. NR latex can be contaminated easily after removal from the tree due to the metabolic activities of microorganism growth on non-rubber components that lead to latex destabilization. The first changes are that the latex coagulates within a few hours. This process is known as spontaneous coagulation. The time required for coagulation depends upon the ambient temperature and the colloidal stability of the latex. The second of the obvious changes is putrefaction with the development of bad odors. The pH of latex decreases and neutralization of the

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charges occurs by hydrolyses of nonrubber substances by the fermentation process of microorganisms and the resultant volatile fatty acids like acidic byproducts. Therefore, appropriate preservatives must be used to maintain the stability and purity of NR latex [2].

Currently, two types of latex preservation methods are used such as short-term preservation system (SATZ) and long-term latex preservation system (LATZ). Where the short-term preservation is used to preserve field NR latex in the stable liquid state for a few hours or days before processing is mainly used in dry rubber production and the long-term latex preservation is applied to enhance the stability during transport and storage of NR latex until the start of the production process. Where the ammonia is used as a good preservative due to its alkalinity and biocidal characteristic and ion stabilizer nature via forming complexes with metal ions [3].

Ammonia is utilized as the sole preservative for the long-term preservative system at high concentrations (0.7%). However, this high concentration of ammonia sole preservative system creates certain drawbacks like discoloration of latex, subsequent coagulation due to the higher acid consumption processing problem with highly alkaline skim latex, and practical problem with handling ammoniated latex by high concentration [4]. Therefore, John, et al have developed secondary preservative systems with low ammonia concentration to overcome the drawbacks of high ammonia sole preservative system for NR latex preservation system [5].

This low ammonia preservative method is known as LATZ in the industry because that preservative system contains ammonia, tetramethyl thiuram disulfide (TMTD), and Zinc Oxide (ZnO). Which become a commercially accepted preservative system in the latex industry, especially in the centrifuged latex industry. On other hand, the amount of non-rubber components is increased in NR latex due to the usage of the plant growth regulator ethephon in rubber cultivation. Hence, the LATZ latex preservative system becomes inadequate preservation of the centrifuged latex process due to its poor latex preservation nature. Not only that, the LATZ system impacts environmental air pollution by ammonia and leads to the production of carcinogenic nitrosamine substances by TMTD [6]. The consideration of an alternative preservative system for the LATZ system is developed to overcome the drawbacks of the LATZ system. Therefore, the new preservative system using a novel chemical will be investigated through this research. Hence, the novel preservative was chosen to utilize as a preservative for field natural rubber latex to replace the traditional Long-Term Latex preservatives, which could replace TMTD in the preservation system. That could attain by the polysulfidic link of novel chemicals, which led to the nature of antimicrobial growth on latex. Where the stability of NR latex and degree of preservation was evaluated using the development of volatile fatty acid (VFA) in latex.

There were many investigations already done in past regarding effective preservative systems and novel alternative preservative systems for NR latex [3,5-16]. Most of the attempts exhibited positive results in the preservation of NR latex. Some of the previous research which discussed the effect of TMTD is given below. Orophin et al. researched with natural rubber latex preservative system by using zinc sulfate, silver nitrate, silver protein, lithium hydroxide, sodium hydroxide, potassium hydroxide, ethanolamine, methyl-4-hydroxybenzoate, and propyl-4- hydroxybenzoate [3]. An advantage of using these preservatives was fewer fumes of ammonia were emitted. This research was carried out to eliminate the carcinogenic nitrosamine from TMTD. The preservative activity of 0.04% w/w $ZnSO_4$ in 0.4% w/w low-ammonia system exhibited effective preserve nature as representing TMTD/ZnO in the ammonia system. The result of $ZnSO_4$ addition was very effective in VFA reduction and kept latex without coagulating for 1 month also showed both particle size and viscosity were almost unchanged. The silver nitrate and silver protein lead color in the latex and coagulate latex within 1 day. Similarly, the addition of methyl-4-hydroxybenzoate and propyl-4-hydroxy- benzoate also coagulated within 1 day. The strong bases, organic bases, and ethanolamine exhibited effective preserve behavior to the latex. They demonstrated that low molecular weight basic compounds could be used in a lower quantity than higher molecular weight basic compounds.

This research also proved that the use of $ZnSO_4$ as a secondary preservative in a non-ammonia system could also enhance microbial activity [3].

Edirisinghe reported a study on the suitability of readily available, low-cost urea to manufacture low ammonia centrifuged NR latex that can use in cast products [15]. urea treated samples exhibited better resistance to thermal degradation than the control sample, which was proved via aging studies. The urea-treated samples also exhibited a reduction in total extractable protein content, which is very useful in latex-based product manufacturing. The microbiological examination also proved that the novel urea preservative could act as a good preservative to NR latex, which could work as a potential substitute for TMTD/ZnO preservative system to reduce the nitrosamines generation. The 0.021 % urea treated latex sample exhibited the best properties even better than the control [15].

Sriwardena et al. did a study to investigate the effect of different preservative systems in the concentrated latex manufacturing industry on the physical properties of the latex crepe made out of them. Where unfractionated and unbleached (UFUB) crepe rubber manufactured from latices preserved with ammonia, TMTD, zinc oxide, and a 1:1 mixture of TMTD and zinc oxide (LATZ) were tested to study the raw rubber properties. The results of this research showed that manufactured UFUB crepe rubber out of either ammonia preserved, ZnO preserved or chemically untreated latices have better resistance to thermo-oxidative degradation than UFUB crepe rubber made out of both TMTD and LATZ preserved latex. That also exhibited that, neither ammonia nor ZnO has any effect on the thermal degradation of crepes produced from ammonia or ZnO preserved latex. The addition of TMTD as a component of the preservative system showed negative effects on resistance to thermo-oxidative degradation and Plastic Reduction Index (PRI) of produced crepe even at very low concentrations. The free radicals generated by dimethyl thiuram monosulfide (DMTMS) that is responsible for PRI reduction via thermal decomposition of TMTD. However, ammonia addition did not affect the raw rubber properties within the ammonia range because the ammonia does not form water-soluble complexes with non-rubbers present in latex such as antioxidants which affect raw rubber properties like Po and PRI [16].

The above studies exhibited the requirement of an alternative preservative for NR latex is needed to eliminate the carcinogenic effect of TMTD and reduce the emission of ammonia fume. Hence, the novel chemical that contains a disulfide link in its chemical structure was planned to utilize as a substitute for TMTD in a low ammonia preservative system. The novel chemical was preferred due to its antimicrobial nature itself, which properties need to preserve latex from the microbial activity on latex particles and maintain the stability of the latex.

Materials and Methods

Field natural rubber latex was collected from the Dartonfield estate of Agalawaththa, belonging to the Rubber Research Institute of Sri Lanka. Ammonia, TMTD, ZnO, and novel chemicals used were of industrial grades and were purchased from general chemical suppliers. Deionized water was used for all the solution preparations. Ammonia was used as a 10% aqueous solution.

In this study, two trials were studied to prove its preserved nature and find the effective concentration of novel preservatives. The first trial was done using the dispersion of a novel preservative that was prepared via the traditional dispersion preparation method by mortar and pestle where water was dispersing medium and the second trial was done. The dispersion preparation method was planned to change and the second trial was done with a novel preservative using a new dispersion preparation method. Where two different dispersions of novel chemicals were prepared such as dispersion 1 and 2 that were included boric acid was used to stabilize the novel chemical and colloidally dispersed in an organic dispersion medium, and glycerin was utilized to increase the stability of effectiveness of preparation. Dispersion 1 was made with Sodium Lauryl Sulfate as a wetting agent to add to the dispersion medium to act as a colloid protective, and dispersion 2 was prepared without using a wetting agent.

Dispersion Preparation Method of Novel Chemical

For the 1st trial, the required amounts of novel chemical, water, and dispersal LR were measured and were mixed by mortar and pestle which was used to reduce the particle size. Then the prepared dispersion was stored in a bottle and the label was pasted on the bottle.

For dispersion 1 of the 2nd trial, the water-free glycerin and boric acid were mixed by heating to a temperature not exceeding 150° C for 20 minutes and let to cool down to room temperature. The novel chemical was added to the mixer. Then the sodium lauryl sulfate was added and mixed well. Finally, the dispersion was poured into the ball mill and allowed particle size reduction.

The dispersion 2 of 2nd trial was prepared by using the same procedure that followed the dispersion 1 preparation, but the sodium lauryl sulfate was not added to the mixer.

The Test Procedures

First, fresh field natural rubber latex samples were collected from the traditional tapping method. Then, the samples were ammoniated with 0.3% of ammonia. Fresh rubber latex with 0.025% TMTD/ZnO preservative added was prepared as a control sample. Other samples were prepared by adding different concentrations of novel chemicals according to Figure 1 and Figure 2 for trials 1 and 2 respectively and a constant amount of 0.0125% ZnO to each. The latex properties of all samples were checked with time (days) via the VFA test, where the DRC, TSC, and alkalinity tests were performed to calculate the VFA value. Finally, the best concentration of the novel chemical for field latex was determined via two trials.

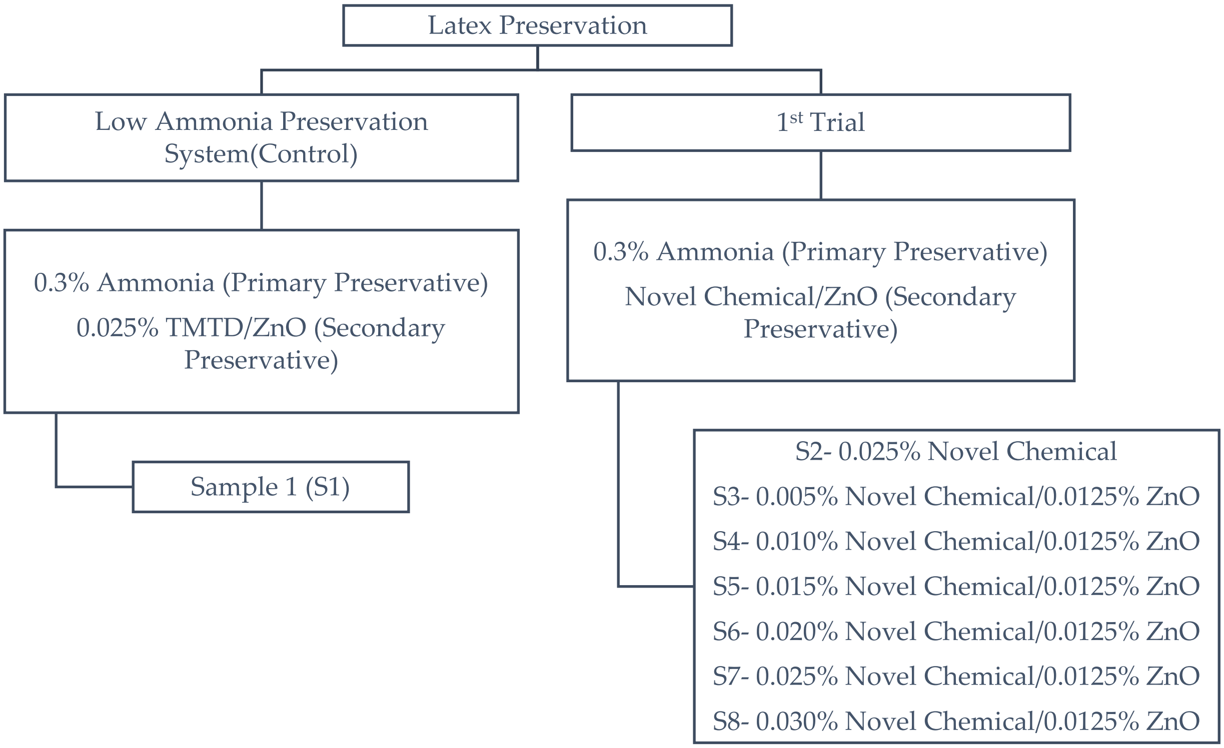


Figure 1- Schematic diagram of trial 1

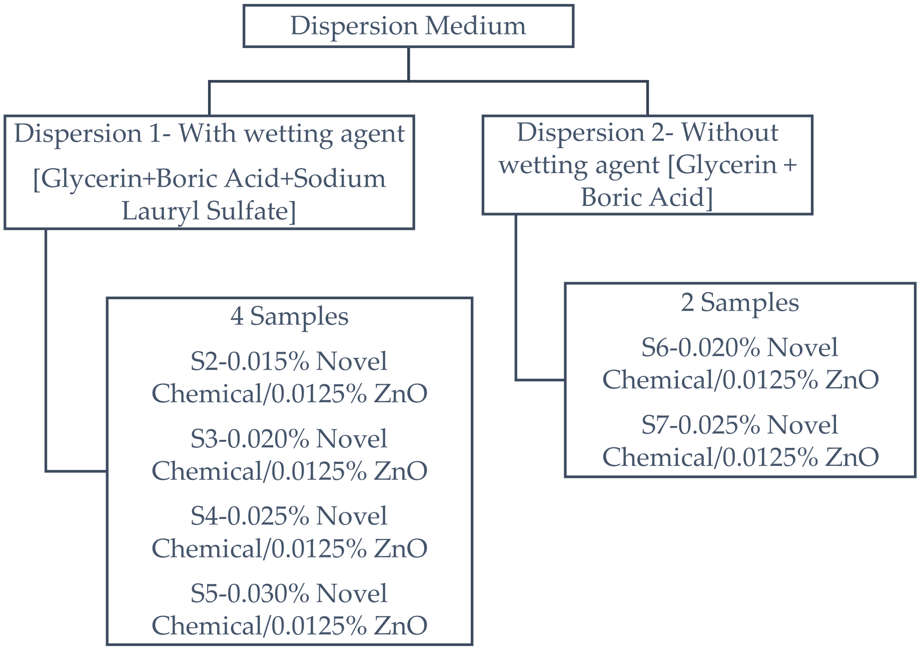
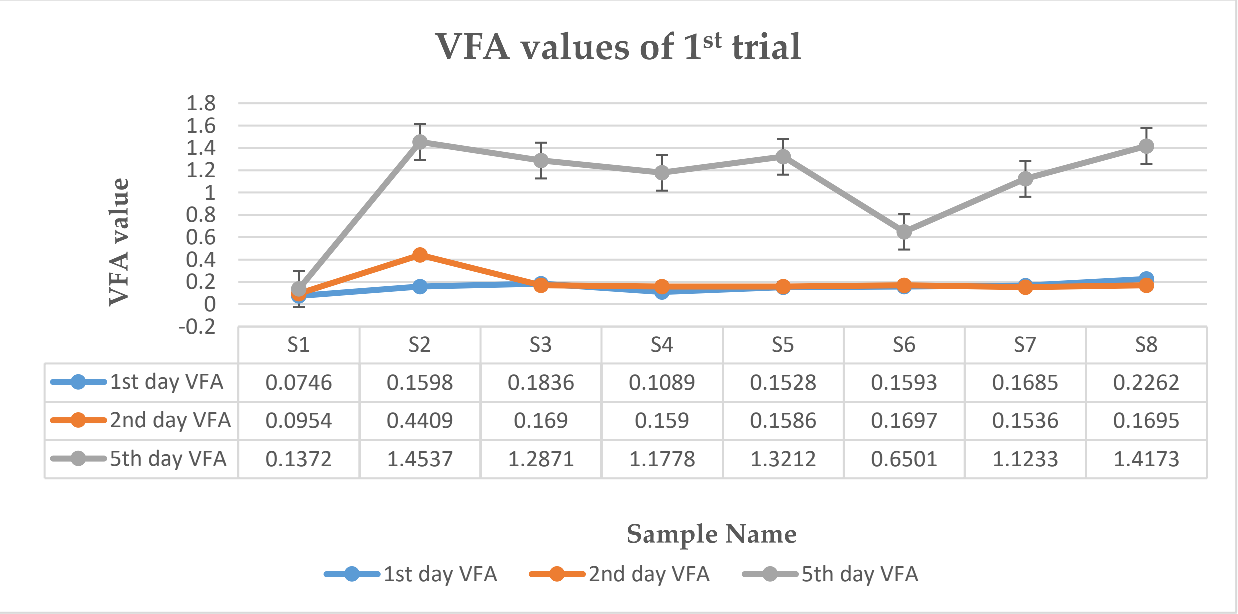


Figure 2- Schematic diagram of trial 2

Results and Discussion

1st Trial

Figure 3 shows the VFA values of the 1st trial below.



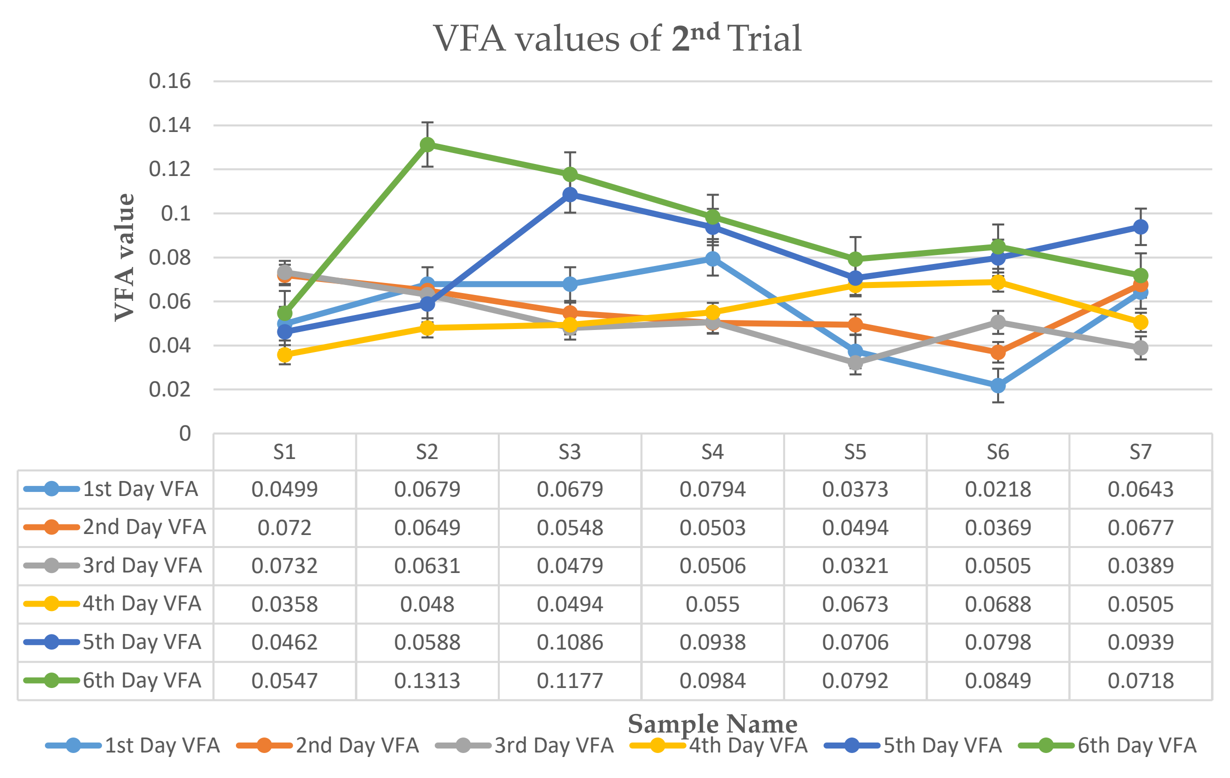
	S1	S2	S3	S4	S5	S6	S7	S8
1st day VFA	0.0746	0.1598	0.1836	0.1089	0.1528	0.1593	0.1685	0.2262
2nd day VFA	0.0954	0.4409	0.169	0.159	0.1586	0.1697	0.1536	0.1695
5th day VFA	0.1372	1.4537	1.2871	1.1778	1.3212	0.6501	1.1233	1.4173

Figure 3- VFA values of the first trial

Usually, 0.1 VFA can be allowable to preserve field latex. According to the graph of 1st trial, the control sample showed good preservative nature until the 5th day, but the samples (S2-S8) preserved by novel chemicals were shown more than 0.1VFA value from the 1st day. However, the trial was continued for 5 days. The low dispersibility nature of novel chemicals in latex led to the low preserve nature, which was identified from the observations. Whereas the traditional dispersion preparation method by mortar and pestle was not effective for novel chemicals. This limited the dispersibility of novel chemicals in latex due to the comparatively large size of particles of the novel chemical suspended in the aqueous medium, where the water was dispersing medium. Hence, the dispersion preparation method was planned to change, and the 2nd trial was done with a novel preservative using a new dispersion preparation method.

Trial 2

Figure 4 shows the VFA values of the 2nd trial below.



	S1	S2	S3	S4	S5	S6	S7
1st Day VFA	0.0499	0.0679	0.0679	0.0794	0.0373	0.0218	0.0643
2nd Day VFA	0.072	0.0649	0.0548	0.0503	0.0494	0.0369	0.0677
3rd Day VFA	0.0732	0.0631	0.0479	0.0506	0.0321	0.0505	0.0389
4th Day VFA	0.0358	0.048	0.0494	0.055	0.0673	0.0688	0.0505
5th Day VFA	0.0462	0.0588	0.1086	0.0938	0.0706	0.0798	0.0939
6th Day VFA	0.0547	0.1313	0.1177	0.0984	0.0792	0.0849	0.0718

Figure 4- VFA values of the second trial

In 1st day observation, the reason behind the long coagulation time may be due to the new dispersion preparation method i.e. glycerin & Boric Acid [Boiling point of Glycerin=290°C, Boric Acid=300°C]. However, the color change flow of precipitation in samples is shown in Figure 5.

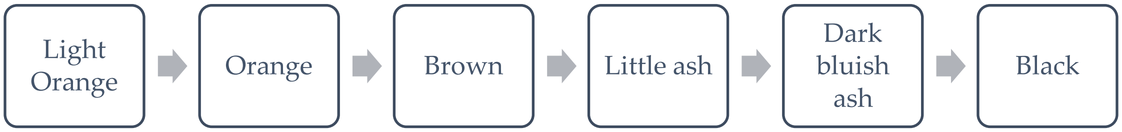


Figure 5- Color change flow of precipitation in samples

In the control sample, there was a VFA drop by 0.037 observed on the 4th day of the trial, which may cause by the extra addition of ammonia after the alkalinity test. The 8th VFA test result may happen by improper froth control in the VFA apparatus.

The S2 sample exhibited a trend in VFA values. The S3 sample exhibited effective preserve nature until the 5th day of trial. After that, S3 was not shown the higher flatulated value in VFA. The S4 sample showed effective preserve nature until the 7th day of trial but exhibited a low VFA value on the 2nd day than on the 1st day, which may be occurred due to the chemical reaction of the novel chemical. The observation on the 5th day of the S4 sample was showed the change in precipitation color of the sample collection bottle at the bottom from orange to brown, which may the indicator of the increment of VFA value. Ash color precipitation was observed on the 7th day, which may the indication of the reaction between the ZnO and the novel chemical. This chemical reaction may lead to a reduction in VFA value on the 7th day. After the 7th day, S4 showed the out-of-limit VFA value.

The S5 sample exhibited effective preserve nature until the 9th day of trial and showed a low VFA value on the 3rd day than on the 2nd day, which may be due to the chemical reaction of the novel chemical. On the 7th day, the sample precipitation color was turned dark blackish ash from brown color, which may an indicator of the early stage of reaction between ZnO and the novel chemical. This reaction has led to a reduction in VFA value and exhibited a favorable increase trend of VFA value until the 9th day.

The S6 sample showed effective preserve nature until the 9th day of trial and showed low VFA value on the 7th day than on the 6th day, which may result in the reaction between ZnO and the novel chemical because the precipitation color changed as ash on the 7th day. However, S6 has exhibited a favorable increase trend in VFA value until the 9th day.

The S7 sample showed effective preserve nature until the 9th day of trial and exhibited low VFA value on the 3rd day than on the 2nd day, which may be due to the chemical reaction of the novel chemical. This also exhibited a low VFA value on the 7th day than on the 6th day, which may result in the reaction between ZnO and the novel chemical, because the precipitation color changed to ash on the 7th day.

According to the combined VFA graph of all samples, S1, S5, S6, and S7 showed good preservative behavior for 9 days. Where both S6 and S7 samples from the 2nd dispersion method (without a wetting agent) of the novel chemical exhibited the best preservative behavior than the 1st dispersion method. 0.020% and 0.025% concentration of the novel chemical (S3 and S4) from the dispersion with wetting agent exhibited preservative behavior for 8 days. A low concentration of the novel chemical (0.015%-Sample S2) was kept latex with good stability for 5 days. However, the samples from dispersion of novel chemicals without a wetting agent have exhibited a marvelous preservative nature to NR latex than the dispersion of novel chemicals with a wetting agent.

Conclusion

The study showed that the novel preservative can effectively replace TMTD/ZnO as a secondary preservative in the ammonia system. Traditional dispersion preparation failed due to the large particle size of the novel chemical. Samples that were prepared without using the wetting agent dispersion method exhibited best preservative behavior than with wetting agent dispersion methods. 0.020% and 0.025% concentration of the novel chemical from the dispersion 1 method (with Glycerin+Boric Acid+Sodium

Lauryl Sulfate) exhibited preservative behavior for 8 days. A low concentration (0.015%) of the novel chemical could keep latex with good stability for 5 days. However, samples that were preserved by prepared novel chemical without using wetting agent dispersion preserved latex for long days than those prepared novel chemical with wetting agent dispersion.

Conflicts of Interest

Further investigation on microbial growth, mechanical stability nature, and film properties could be carried out to field NR latex in the future. Moreover, the preserved nature and field performances of novel preservatives on concentrated NR latex also could be investigated in the future.

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