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Blending of High VFA Latex Concentrate with Low VFA Latex Concentrate

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Low ammonia (LA) centrifuged latex of higher volatile fatty acid (VFA) values was blended with that of lower values at different blend ratios. The most important latex characteristics of these blends, namely VFA number, KOH number and MST were tested over a period of time at regular intervals. It was found that centrifuged latex with different VFA values could be blended to obtain a predetermined intermediate VFA value in the final blend. VFA number in the blends as well as in the two unblended latex samples increased gradually after an induction period of 40-50 days. The rate of increase of VFA number was more pronounced in the blends containing higher proportions of high VFA centrifuged latex. A formula was proposed to estimate the VFA number of the final latex blend using the VFA numbers of the initial components of the latex blend. The same formula could be used to estimate the quantity of latex from each latex component to be blended to obtain a targeted VFA value in the final latex blend. After an initial high rate of increase of KOH number in the blends prepared from fresh latex, the rate of increase reduced drastically to almost zero with the increase of maturity. The development of mechanical stability time (MST) of the blends over time was observed to be at par with the development of KOH number barring few exceptions.

Keywords: blends; centrifugation; proteins; rubber; latices

Natural rubber (NR) latex obtained from *Hevea brasiliensis* tree has a dry rubber content (DRC) generally varying between 30% and 35%. Latex compounds prepared using latices with such low DRC have a lower pick up on the former when making dipped products and foaming is difficult in the manufacture of foam rubber. Further, the water content in NR field latex is double the quantity of rubber in it thus making transport of latex uneconomical. To overcome the above problems, field latex is concentrated to a DRC of 60% or more. The common method currently used for concentration of latex is centrifuging. Most of the heavier non rubber substances are separated in this process whilst the product obtained is uniform since field latex from different sources is bulked and homogenised before centrifuging.

Latex after centrifuging is well preserved either with ammonia alone at 0.6 % (w/w) or

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with ammonia at 0.2 % (w/w) together with a secondary preservative such as TMTD/ZnO at 0.025 % (w/w). Depending on the ammonia concentration in latex, there are two types of latex namely high ammonia (HA) and low ammonia (LA). The most common secondary preservative is TMTD/ZnO and the latex is then known as LATZ latex.

NR field latex and its concentrate are characterised by several quality parameters; the most important of these parameters are VFA number and DRC. Out of the two parameters mentioned, the VFA number is the most critical since it indicates the state of preservation of latex. The acceptance or rejection of latices by most product manufacturers is decided mainly by this parameter.

It is well known that volatile fatty acids are generated in NR latex due to bacterial action if latex is not properly preserved. Bacteria interact with carbohydrate substrates especially sugars such as sucrose[1], glucose[2], galactose and fructose[3] present in NR latex during their proliferation and form VFA such as formic acid and acetic acid; the latter is more prominent[2]. In the process of centrifuging of NR field latex, a greater part of the non rubber substances including sugar is separated from the cream and removed with the skim. Nonetheless, even a very little portion of sugar remaining in the concentrate may be sufficient to generate VFA to a significant level, unless latex is properly preserved. Further, amino acids such as alanine and glutamic acid may act as substrates for VFA formation probably *via* glucose-amino complex[2]. Ammonia, a bactericide, used as the common preservative reacts with glucose and fructose in latex resulting in aldehyde ammonia or keto ammonia complex, which is less amenable for bacterial breakdown[1]. However, VFA may still build-up in latex due to the activities of a wide variety of enzymes such as proteases and lipases indigenously present in latex[2]. An enzyme inhibitor such as TMTD[1] can prevent the VFA build-up in latex. According to the studies of Lowe[4], after a short induction period, VFA number in field latex increases over a period of few days, until a stage is reached where only a very little further increase occurs. The reason given for the decline of the rate of formation of VFA is either due to exhaustion of carbohydrate substrates or due to deactivation of enzymes.

After manufacture, concentrated latex is well preserved and hence the VFA number hardly changes. Nevertheless, there is a possibility of VFA number increasing to higher levels due to problems in the preservation of latex. Further, the complete killing of bacteria in field latex at a relatively late stage does not necessarily prevent VFA build-up since enzymes capable of producing VFA can be released from the dead cells, unless they are deactivated by enzyme poisons or inhibitors[1]. In such instances, the latex is devalued for its inferior quality. To upgrade the quality of such latex to acceptable quality levels, one option is the progressive dilution of latex and re-centrifuging in order to reduce further the ratio of non rubber substances to rubber in the latex. VFA in latex can be reduced to virtually immeasurable levels after two centrifugations[5]. One of the disadvantages of this process is the loss of natural colloid stabilisers as a consequence. The other inherited disadvantages of the process are the cost factor and the loss of rubber in skim, hence the process is very prohibitive. Another possible option is to blend such high VFA latex with low VFA latex concentrate so that the VFA level in the blend may be able to be kept within acceptable levels for use in product manufacture.

Two other properties which are generally monitored during maturation of centrifuged latex are KOH number and MST. KOH number is the number of grams of KOH

equivalent to total fatty acid radicals combined with ammonia in latex containing 100 g of total solids while VFA number is defined as the number of grams of KOH equivalent to volatile fatty acids in latex containing 100 g of total solids. KOH number too increases during maturation due to the formation of both volatile fatty acids and higher fatty acids. Higher fatty acids are formed in NR latex due to the hydrolysis of phospholipids which is accelerated after ammoniation of latex. With the generation of higher fatty acids and adsorption of them to the surface of the rubber particles, the number of negative charges around the rubber particles increase and as a result, the MST also increases. In addition to the higher fatty acids naturally generated in latex, it is a common practice to incorporate a small concentration of fatty acid soaps into centrifuged latex just after manufacture in order to 'boost' the MST development. Excessive addition of this soap can also be detected with the determination of KOH number.

Some studies on the blending of high VFA and low VFA latex concentrates have been carried out[6] but the VFA value in high VFA latex concentrate used in the study was only 0.044. This paper reports with special emphasis on VFA number, the results of a series of studies conducted on quality variation of centrifuged latex blends of high VFA and low VFA latex having different higher and lower VFA values and different maturities in high and low VFA latex components used in the blends.

MATERIALS AND METHODS

LATZ centrifuged latex with both high VFA number and low VFA number with different maturity levels was obtained from Ms. Lak Latex (Pvt) Ltd. at Badureliya, Sri Lanka. High VFA latex was defined in this study as those batches of latex concentrate having a VFA number more than 0.05 whilst those having a VFA number less than 0.05 were regarded as low VFA latex.

All the chemicals used for analysis were of analytical grade.

Latex blends used in this study are shown in *Table 1*. The latex after blending was thoroughly mixed by shaking the containers well. Latex was stored at ambient temperature between 25 - 30ºC.

Tests on Latex Blends :

Total solids content – ISO 124 : 1997 (E)
Dry rubber content – ISO 126 : 1995(E)
VFA number – ISO 506 :1992(E)
Alkalinity – ISO 125 :1990(E)
KOH number – ISO 127 : 1995 (E)
Mechanical stability time – ISO 35 : 1995(E)

Three trials were carried out in blending latices with different maturities. Both high VFA and low VFA LATZ latex taken for the first trial was fresh with seven days maturity. For the second trial high VFA latex was fresh with two days maturity and low VFA latex was fresh with seven days maturity. For the third trial both high VFA and low VFA latex were well matured for 60 days and 80 days respectively. Latex blends were immediately tested for total solids content (TSC), DRC and alkalinity. Testing of latex for VFA number, MST and KOH number were continued at regular intervals as follows:

First trial - up to the 8th week
Second trial - up to the 9th week
Third trial - up to the 24th week

The following equation was derived from an equation used by Utracki[7] for polymer blends in order to calculate the predicted VFA values in the blends.

$$VFA_b = \varphi_h VFA_h + \varphi_l VFA_l + \varphi_h \varphi_l \varsigma \quad \ldots 1$$

where,

VFA_b = VFA number of the latex blend
VFA_h = VFA number of high VFA latex concentrate
VFA_l = VFA number of lowVFA latex concentrate
φ_h = Weight fraction of high VFA latex concentrate in the blend
φ_l = Weight fraction of low VFA latex concentrate in the blend
ς = Interaction parameter

Assuming there is no interaction between the two components of the blend, value of ς becomes negligible and therefore the value for $\varphi_h \varphi_l \varsigma$ too becomes negligible, thus the equation could be rewritten as follows;

$$VFA_b = \varphi_h VFA_h + \varphi_l VFA_l \quad \ldots 2$$

RESULTS AND DISCUSSION

The TSC and DRC of latex blends are shown in *Table 2*. The initial VFA number of all the blends is tabulated in *Table 3*. The predicted values for VFA number of the blends calculated using *Equation 2* are also tabulated in the same *Table 3*. The results shown in *Table 3* show that high VFA latex can be blended with low VFA latex to obtain a desirable VFA number in the blend. The proportion to be blended depends on the desirable VFA number of the final blend to be used in the particular application and the VFA number of the initial latex concentrate. The comparison of experimentally determined VFA number with the predicted VFA number in *Table 3* and the percentage deviation from the predicted VFA number depicted in *Table 4* clearly showed that the experimentally determined VFA numbers are more or less identical with the predicted VFA numbers. Therefore, it infers that the equation used for the prediction of VFA values in the blends and also the assumption made therein is correct. Hence, it is possible that latex having different VFA numbers can be blended to obtain a pre-determined value in the blend within a reasonable accuracy of ±5% using the proposed equation.

In our experiments, all the blends were kept in air tight containers to prevent the escape of ammonia, the primary preservative, from the latex blends. The variation of VFA number of the blends was studied during storage of these latex blends. *Figure 1* shows that VFA number of all the latex blends increased only very slightly with maturity throughout the test period of 48 days in the first trial. In the second and third trials latex with different VFA numbers were used and the test period was extended to 57 days in the second trial and 170 days in the third. The variation of VFA number in the second trial is shown in *Figure 2* and that in the third trial is shown in *Figure 3*. It is clear from *Figures 2* and *3* that after an induction period of about 40-50 days, the VFA number increased at different rates in different periods. To investigate if the alkalinity has any influence on the increase of VFA number, the variation of alkalinity too was studied in the third trial which is shown in *Figure 4*. It showed that the alkalinity also

TABLE 1. BLEND RATIOS OF HIGH VFA AND LOW VFA LATEX

Description	Weight percentage					
Sample label	A	B	C	D	E	F
High VFA	100	60	40	20	10	-
Low VFA	-	40	60	80	90	100

TABLE 2. TSC AND DRC OF LATEX BLENDS

Sample no.	First trial		Second trial		Third trial	
	TSC (%)	DRC (%)	TSC (%)	DRC (%)	TSC (%)	DRC (%)
A	62.30	60.90	63.02	61.80	61.20	59.60
B	62.22	60.81	62.54	61.05	61.65	60.00
C	62.00	60.41	62.23	60.90	61.80	59.80
D	61.71	60.10	62.23	60.59	61.90	60.50
E	61.57	59.80	62.21	60.50	62.00	60.20
F	61.52	59.70	62.05	60.63	61.80	60.20

TABLE 3. VFA NUMBER OF LATEX BLENDS ANALYSED BY THE ISO TEST METHOD AND THE PREDICTED VALUES CALCULATED USING *EQUATION 2*

Sample label	High VFA/ low VFA (by weight)	VFA Number					
		Trial 1		Trial 2		Trial 3	
		Actual	Predicted	Actual	Predicted	Actual	Predicted
A	100/0	0.067	0.067	0.059	0.059	0.109	0.109
B	60/40	0.051	0.050	0.050	0.045	0.075	0.078
C	40/60	0.043	0.042	0.043	0.038	0.065	0.062
D	20/80	0.036	0.033	0.038	0.031	0.053	0.047
E	10/90	0.031	0.029	0.032	0.028	0.042	0.039
F	0/100	0.025	0.025	0.024	0.024	0.031	0.031

TABLE 4. DEVIATION OF VFA NUMBER OF LATEX BLENDS FROM PREDICTED VALUES

Sample label	High VFA/ low VFA (by weight)	VFA Number					
		Trial 1		Trial 2		Trial 3	
		Deviation	% Deviation	Deviation	% Deviation	Deviation	% Deviation
A	100/0	0.000	0	0.000	0	0.000	0
B	60/40	+0.001	+1	+0.005	+5	-0.003	-3
C	40/60	+0.001	+1	+0.005	+5	+0.003	+3
D	20/80	+0.003	+3	+0.007	+7	+0.006	+6
E	10/90	+0.002	+2	+0.004	+4	+0.003	+3
F	0/100	0.000	0	0.000	0	0.000	0

slightly decreased during this period probably due to the escape of ammonia during regular opening of the containers for sampling of latex for testing. According to the recommendations, the minimum ammonia level for preservation of latex with low ammonia/TMTD/ZnO system is 0.2%[8]. This minimum level had been maintained in all the blends except A and B (see *Table 1*), throughout the test period. Therefore, it is clear that the increase of VFA number after about 50 days is not due to the reduction of ammonia level in latex.

The possible reasons for the increase of VFA number after an induction period of 40-50 days can be explained by referring to the work done by Lowe[4]. According to his studies, after a short induction period the VFA number

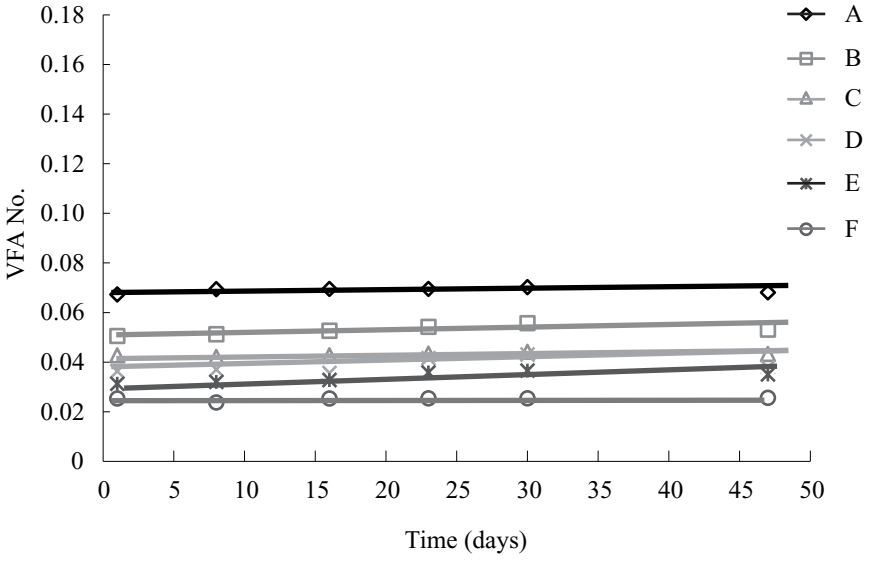

Figure 1. Variation of VFA No. of latex blends with time (1st trial).

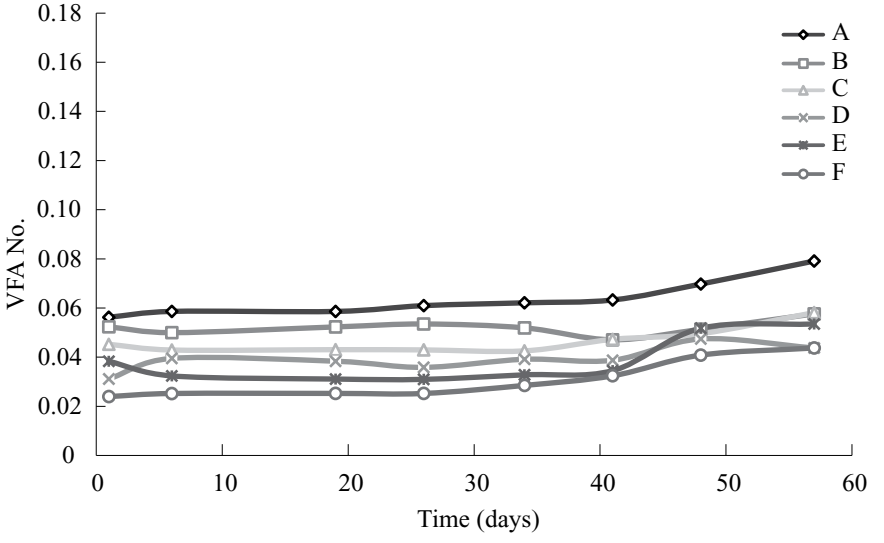

Figure 2. Variation of VFA No. of latex blends with time (2nd trial).

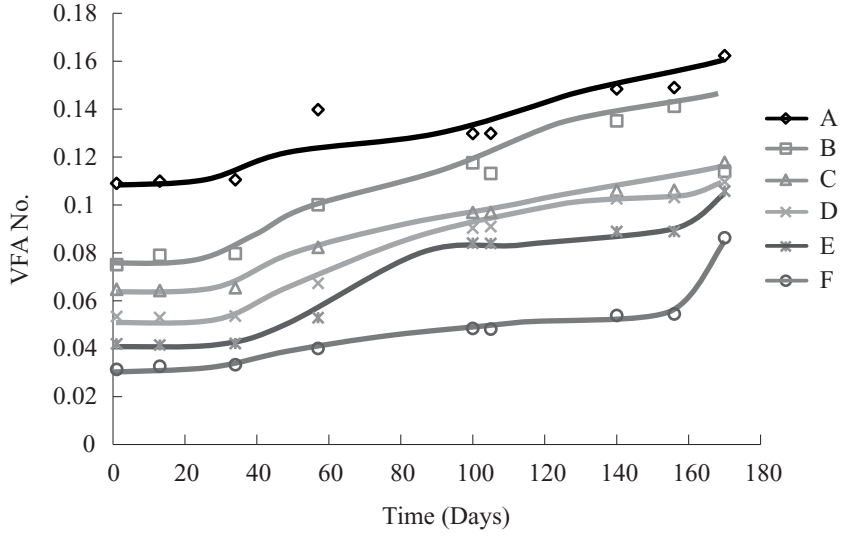

Figure 3. Variation of VFA No. of latex blends with time (3rd trial).

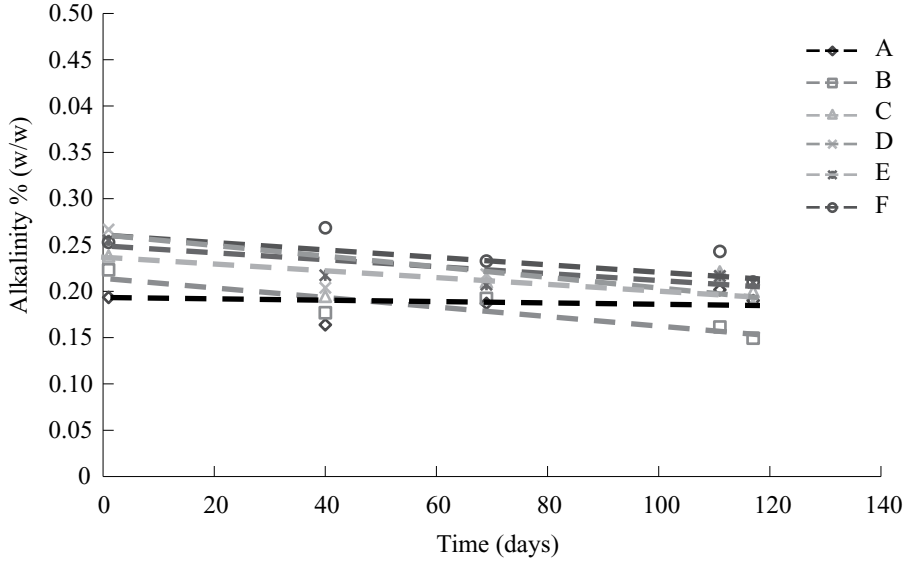

Figure 4. Variation of alkalinity of latex blends with time (3rd trial).

in field latex increases rapidly over a period of a few days, until a stage is reached after which very little further increase occurs which may be the result of an enzyme catalytic process. The eventual decline of the rate of formation of VFA to effectively zero had been explained by Lowe either due to exhaustion of substrate for the process or deactivation of enzymes. The data obtained in our third trial over a period of 170 days showed that the rate of formation of VFA in the blends of latex concentrates had not declined even after 24 weeks. However, a notable difference was observed in the rate of formation of VFA between the blends and the latex concentrate which had only low VFA latex component in which the rate was very low compared to all other blends. The most probable reason for the higher rate of increase of VFA number in latex blends containing high VFA latex may be the release of enzymes from the dead cells of bacteria[1] abundantly available due to increased bacterial proliferation which may have occurred in high VFA latex to react with the substrates in the absence of adequate concentration of TMTD, an enzyme poison, in the latex blends. Another reason for VFA formation can be explained from the observations of Lowe[2] who has pointed out that amino acids such as alanine and glutamic acid may also be a substrate for VFA formation. He has also suggested that the formation of these types of amino acids by the hydrolysis of proteins leads to the production of glucose-amino acid complex which 'triggers off' VFA formation. On the other hand, low VFA latex might have been properly preserved at an early stage so that bacterial proliferation may have been very minimal in it and hence the rate of increase of VFA number was lower than that in other blends which had high VFA latex component in them. According to another theory, the development of VFA after a period of 40-50 days can be attributed to the onset of activity of anaerobic bacteria[9,10] formed after about 6-7 weeks in the absence of air in the containers which were kept in airtight containers. Therefore, it can be suggested that the most probable reason for the VFA development of latex concentrates after 40-50 days could be the combined effect of the formation of amino acids by the activity of anaerobic bacteria and the enzyme activity due to the release of enzymes from dead bacteria cells. However, if anaerobic bacteria was formed it should have been a special species which resisted the action of bactericides used in these experiments. The presence of anaerobic bacteria was not studied.

It has been shown that the aeration of latex in storage by pumping has no effect on VFA production of ammonia preserved concentrated latex[9] and in fact the anaerobic bacteria may be annihilated due to aeration[9,12]. Therefore, aeration may be done to control VFA development by the action of anaerobic bacteria, which in turn, will have the least adverse effect on MST development in latex concentrate. This may be the reason why the tankers should not be completely filled and a little air space should be kept as suggested by Collier[9] to allow MST development by keeping the VFA build-up at its minimum.

Figure 5 shows the variation of KOH number of latex blends in the first trial. It is apparent that although the VFA number was almost constant with a very slight gradual increase throughout the test period, there was a gradual increase of KOH number after 10-15 days in all the blends except the blend which had only high VFA latex component in it. The rate of increase of KOH number of the latter was observed to be the least whilst that was the highest in the blend which had only the low VFA component. The increase of KOH number was up to values between 0.78 and 0.83 from values in the region of 0.71. Variation of KOH number in the second trial is shown in *Figure 6* and that in the third trial is shown in *Figure 7*. The comparison of

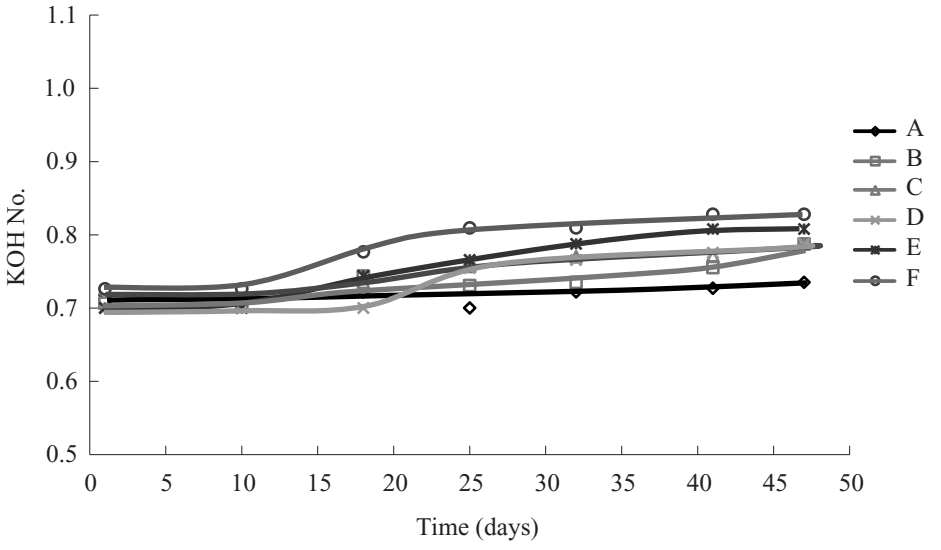

Figure 5. Variation of KOH No. of latex blends with time (1st trial).

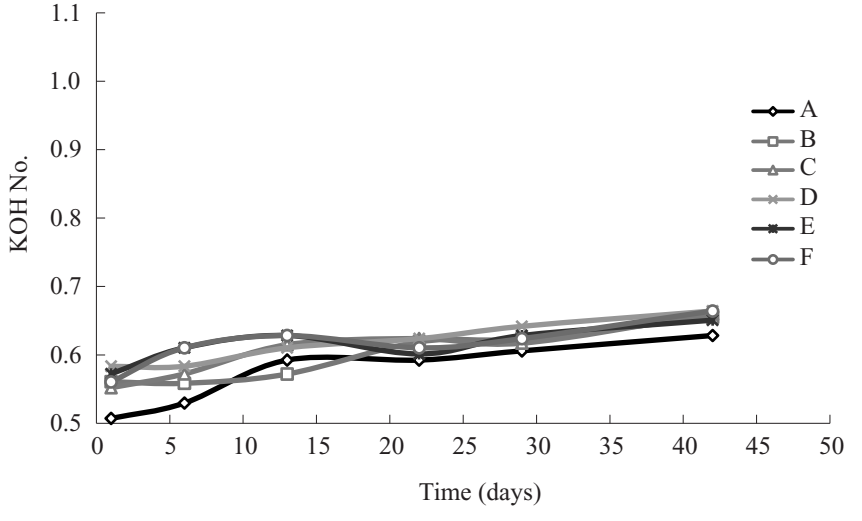

Figure 6. Variation of KOH No. of latex blends with time (2nd trial).

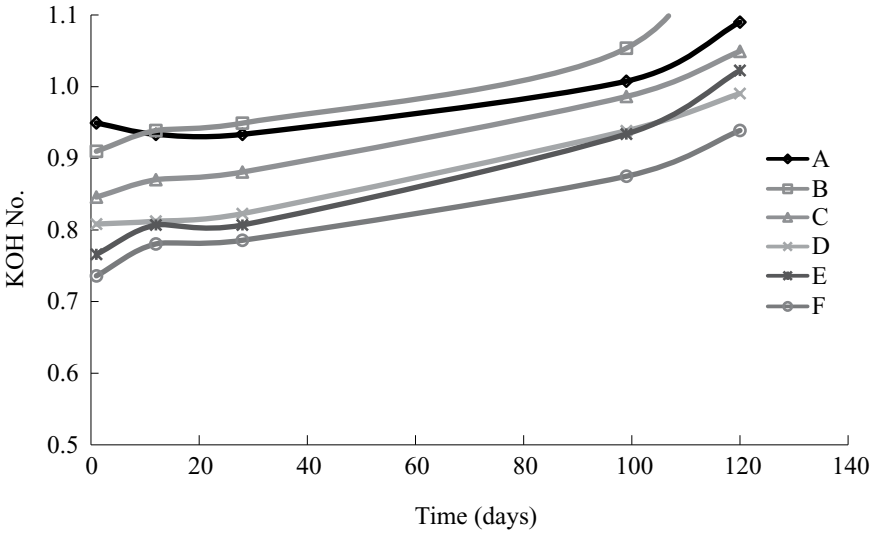

Figure 7. Variation of KOH No. of latex blends with time (3rd trial).

variation of KOH number in the third trial with those in the first and second trials indicated that it was only a very slight increase in the third trial. This may have been due to the high maturity of latex concentrate used in the third trial which had a higher initial KOH number of above 0.8. The patterns of development of KOH number in the three trials as shown in *Figures 5*, *6* and *7* indicated that after an initial high rate of increase of KOH number in immature latex concentrate (KOH number = 0.5-0.6), it reduced drastically to near zero with the maturation of latex concentrate (KOH number of matured concentrate = 0.8-0.9).

Figure 8 shows how the MST of the latex blends in the first trial varied with time and it showed a gradual increase of up to 800 - 1000 s from values of about 400 to 600 seconds. The latex used in this trial was somewhat matured as can be presumed from the initial KOH value of around 0.71 and from the MST value of above 1000 s in high VFA latex concentrate and therefore there was no drastic improvement of MST can be seen in the blends containing high proportion of high VFA latex. However, in the second trial, the latex was comparatively very fresh as can be seen from the initial lower KOH values in *Figure 9* and the lower MST values between 150 and 700 s, a drastic improvement of MST could be seen in latex blends which contained a high proportion of low VFA latex component. The improvement of MST was very minimal in the blend containing 100% high VFA latex component in this trial. In contrast, there was only a very slight improvement of MST of the blends in the third trial as can be seen in *Figure 10*. In this third trial, both low VFA and high VFA latex taken for the preparation of blends had been highly matured as can be seen from the initial KOH number of around 0.8 and the initial MST above 1000 s and therefore the rate of MST development was very low. The variations of MST shown in the three trials were observed to be somewhat at par with the development of KOH number of the blends in those three trials barring few exceptions

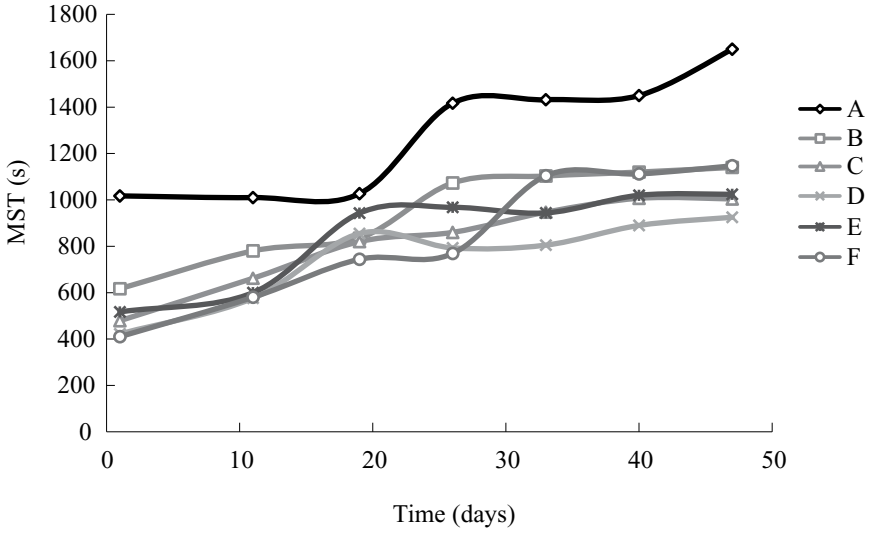

Figure 8. Variation of MST of latex blends with time (1st trial).

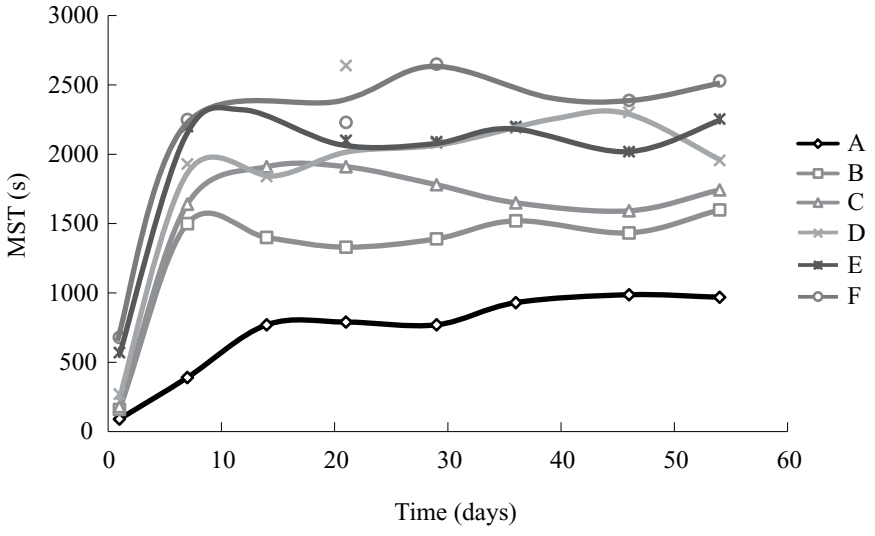

Figure 9. Variation of MST of latex blends with time (2nd trial).

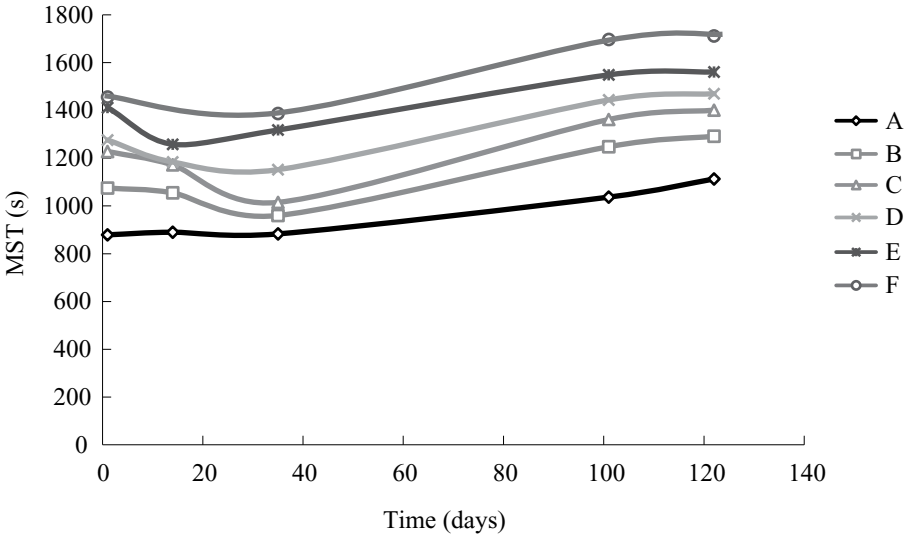

Figure 10. Variation of MST of latex blends with time (3rd trial).

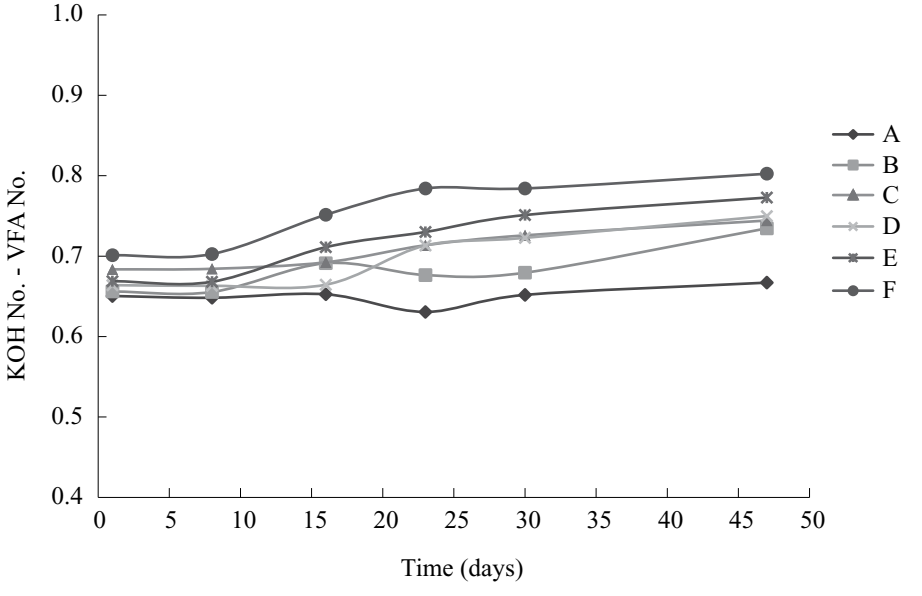

Fig 11. Variation of (KOH No. - VFA No.) with maturity (1st trial).

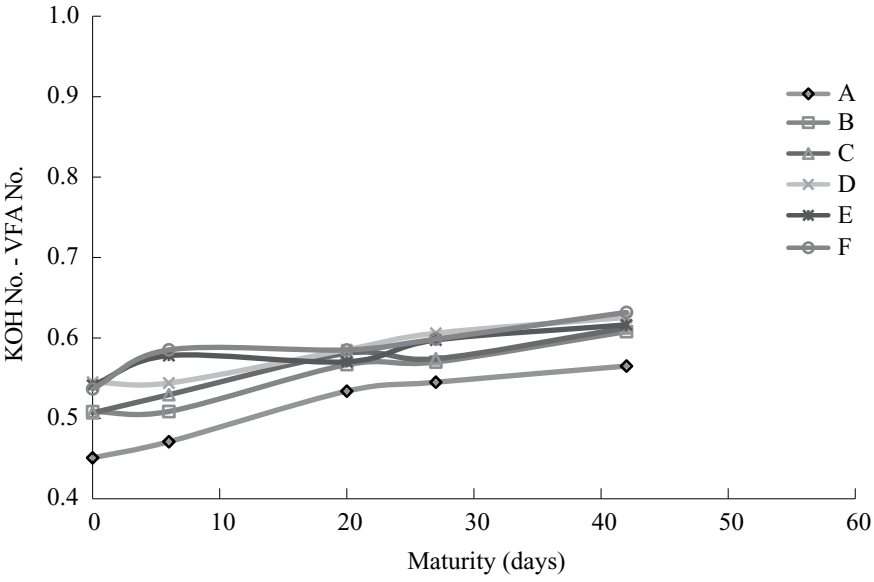

Figure 12. Variation of (KOH No -VFA No) with maturity (2nd trial).

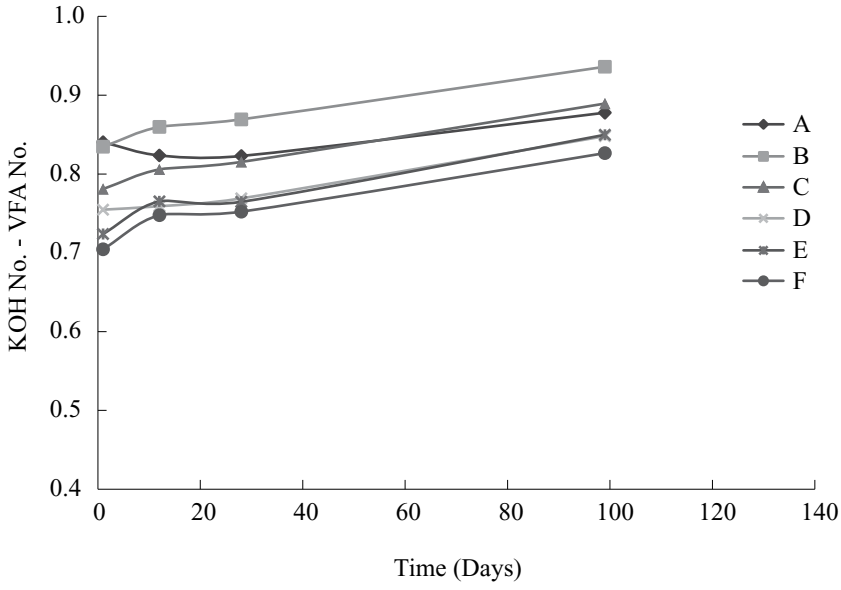

Figure 13. Variation of (KOH No - VFA No) with maturity (3rd trial).

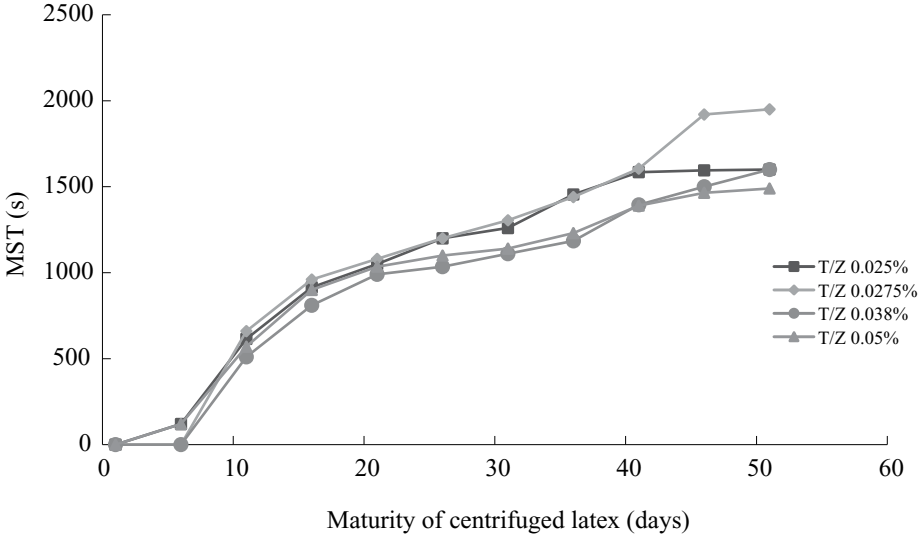

Figure 14. Effect of T/Z dose in field latex on MST development in centrifuged latex.

(compare *Figure 8* with *Figure 5*, *Figure 9* with *Figure 6* and *Figure 10* with *Figure 7*). The development of MST is due to the formation of higher fatty acids (HFA) which are adsorbed to rubber particles enhancing the stability of particles. The development of HFA can be seen in *Figures 11, 12* and *13*. When the MST development is compared with KOH development or HFA development, it can be seen that MST development is not necessarily related with KOH/HFA development. The reasons for these observations can be explained by the fact that non volatile fatty acids formed by transamination of amino acids[13] and long chain fatty acids formed by hydrolysis of phospholipids as well as the VFA formed in latex influence the MST of ammoniated latex. Furthermore, the development of MST was observed to be affected by the dose of T/Z incorporated into field latex as the secondary preservative as can be seen in *Figure 14*. The KOH development in centrifuged latex made from field latex incorporating different doses of T/Z under this study was observed to be more or less equal thereby confirming that the differences in MST development was not merely due to different levels of KOH developed, but other factors are also involved.

CONCLUSIONS

High VFA latex can be blended with low VFA latex in order to upgrade the quality of high VFA latex without any detrimental effect on the properties of the resulting blend such as MST and KOH. The proportion of high VFA latex blended with low VFA latex depends on the standards set by the buyer/product manufacturer. However, VFA development was faster in the blends containing higher proportions of high VFA latex probably due to the release of enzymes from dead bacteria cells contained in high VFA latex component. The following equation was found to be suitable to estimate the VFA number of the latex blends prepared from two different latex concentrates having different VFA numbers. It could also

be used to estimate the quantities of high VFA and low VFA latex to be blended to obtain a targeted VFA value in the latex blend.

$$VFA_b = \varphi_h VFA_h + \varphi_l VFA_l$$

where,

VFA_b = VFA number of latex blend
VFA_h = VFA number of high VFA latex concentrate
VFA_l = VFA number of low VFA latex concentrate
φ_h = Fraction of high VFA latex concentrate in the blend
φ_l = Fraction of low VFA latex concentrate in the blend

VFA number of centrifuged latex was constant up to a period of 40-50 days when kept in air-tight containers and thereafter gradually increased. The development of MST in the blend was somewhat par with the development of KOH number, but not necessarily related with it.

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