VOLATILE ACIDS AND THE QUALITY OF CONCENTRATED NATURAL LATEX

By

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A simplified procedure for determining volatile fatty acids in ammoniated latex is presented. Specific conductivity can be used to indicate an approximate value of VFA number. Volatile acids can be formed in field latex before and after ammoniating, the extent depending on a number of factors including time of ammoniation, amount of ammonia added and period of storage. A small amount of formaldehyde added before ammoniation delays the development of volatile acids. The VFA No. of a 60 per cent d.r.c. concentrate lies between one third and one half of the VFA No. of the field latex from which it is prepared and it is shown that the presence of moderate and high concentrations of volatile acids in the concentrate is associated with inhibition of the normal increase in mechanical stability on storage. Low grade concentrate can be purified by recentrifuging and its mechanical stability increased.

Much attention has been paid to the variation in the properties of natural rubber latex [1, 2, 3, 4], and important among the causes of variation are the acidic products of decomposition which have considerable effects on conductivity[1] and mechanical stability[5]. The importance of acidic constituents on the chemical stability of latex compounded with zinc oxide has also been well discussed [6, 7, 8].

Until recently the acidic content of latex has usually been determined by the KOH No. test which estimates most of the acidic ions in latex but has the disadvantage that no differentiation is made between the long chain stabilising acids and the short chain destabilising ones[6]. In 1953, PHILPOTT and SEKAR[9] showed that the short chain volatile fatty acids can be determined by steam distillation of serum from acid coagulated latex. They have indicated that volatile acids develop rapidly in fresh and lightly ammoniated latex and that the presence of volatile acids affects the properties of concentrated latex.

The determination of volatile fatty acids has been found to be a useful method for controlling the quality of latex concentrate in commercial production. In this paper, effects of volatile acids on the properties of ammoniated, centrifuged concentrate and factors affecting the development of volatile acids are discussed.

EXPERIMENTAL

The determinations of dry rubber content, total solids, ammonia and KOH No. were carried out using the methods recommended by the American Society for Testing Materials (ASTM)[10]. Mechanical stability was determined at a dilution of 51.5 per cent total solids using the 1951 ASTM method[11] and the Klaxon Stability Apparatus[12].

Specific conductivity was measured at 30°C using a Cambridge Conductivity Bridge which is based on the Wheatstone Bridge principle.

The method employed for volatile fatty acid number (VFA No.) was a simplification of the macro scale, constant volume method described by Philpott and Sekar[9]. For 118 estimations a marked relationship was found to exist between the titre value of the first 50 ml of distillate (x) using 0.01N sodium hydroxide and the calculated titre value for the total volatile fatty acids in 50 gm of latex (y). The regression equation was $y = 1.43 + 9.18x$. About half an hour was required for this simplified method compared with about two hours for the full determination. Details of the method used are as follows:

> Weigh 50 gm of latex of known total solids content. Add 100 ml. of distilled water, then slowly add 20 ml of 5N sulphuric acid mixed with 5 ml of distilled water to coagulate the latex. Filter the serum through a Buchner funnel. Pipette 100 ml of clear serum into the distilling flask and add 50 ml of distilled water. Add a drop of anti-foaming agent (Siotol AF). Steam distill at constant volume and collect 50 ml of distillate in 15 minutes. Titrate the distillate with 0.01N sodium hydroxide, using phenolphthalein as indicator.
>
> Determine a blank titration of 50 ml of distillate from 20 ml of 5N sulphuric acid and 130 ml of distilled water with a drop of anti-foaming agent.

CALCULATION

Subtract the blank titre value from the serum distillate titre value to give a corrected titre value (x). Calculate the titre value (y) of volatile acids in 50 gm of latex from the equation:

$$y = 1.43 + 9.18\,x$$

The VFA No. is usually reported as gm of potassium hydroxide per 100 gm total solids. Therefore:

$$\text{VFA No.} = \frac{y \times 0.000561 \times 100 \times 2}{\%\ \text{total solids}}$$

$$= \frac{0.1122 \times y}{\%\ \text{total solids}}$$

All determinations and observations were made in duplicate and each experiment was repeated on a separate bulk of latex collected on a different day.

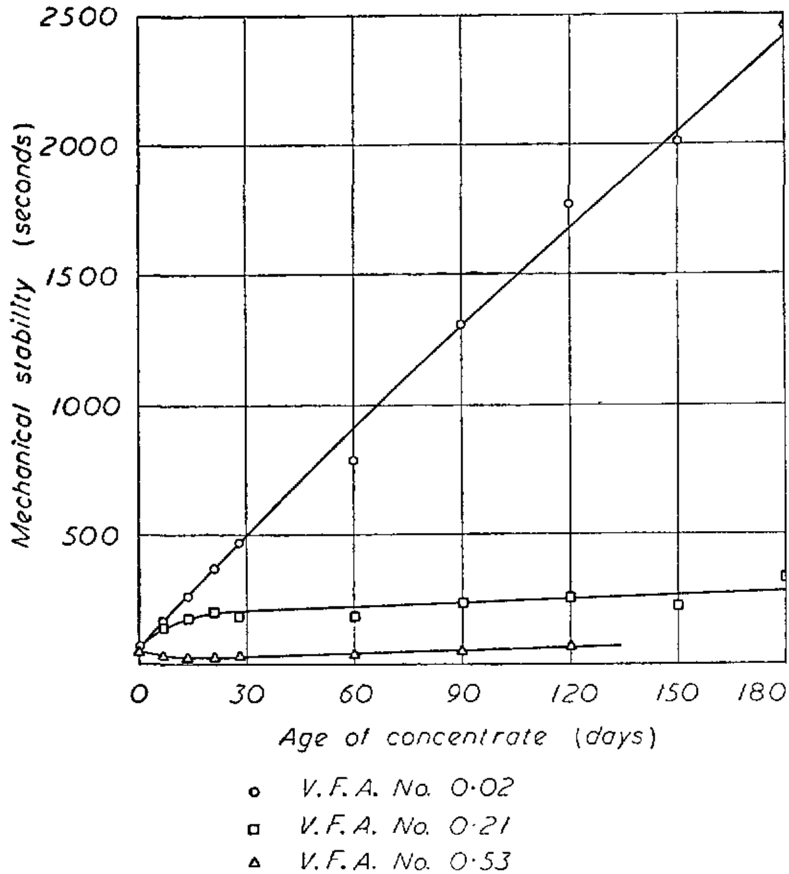

Figure 1. Increase in mechanical stability upon storage of concentrates made from Tjir 1 latex at three levels of VFA No.

VOLATILE ACIDS AND STABILITY

Field latex was collected from two sources at the Rubber Research Institute Experiment Station, namely, latex of clone Tjir 1 and old mixed clonal and seedling latex. The latices were ammoniated to 0.3% NH_3 and four gallon lots were centrifuged immediately. Other samples were retained until the VFA No. had reached values of about 0.2, 0.4, 0.8 and 1.0 before centrifuging. Concentrates were immediately ammoniated to over 0.7% NH_3. Data on the development of volatile acids and initial tests on the concentrates are given in TABLE I.

Samples of the concentrates were stored in winchester quart bottles and tested after 7, 14, 21, 28, 60, 90, 120, 150 and 180 days. Storage effects on mechanical stability are shown in *Figures 1* and *2* and changes in other properties are given in TABLES II and III.

TABLE I: PREPARATION OF CENTRIFUGED CONCENTRATE WITH INCREASING VFA NO.

Age of field latex when centrifuged	Field latex		Concentrate (tested on the day of centrifuging)					
	VFA No.	NH_3 (%wt)	Total solids (%wt)	NH_3 (%wt)	VFA No.	KOH No.	Specific conductivity mhos $\times 10^3$	Mechanical stability (seconds)
1. Latex from clone Tjir 1 (41.66% t.s.)								
(a) 6 hours	0.03	0.33	60.46	0.72	0.02	0.34	3.55	65
(b) 5 days	0.35	0.26	59.23	0.78	0.21	0.71	4.87	68
(c) 11 days	0.88	0.36*	57.43	1.08	0.53	1.24	6.87	53
2. Mixed clonal and seedling latex (42.32% t.s.)								
(a) 6 hours	0.03	0.40	60.11	0.83	0.02	0.37	3.27	63
(b) 3 days	0.18	0.36	62.12	0.76	0.12	0.52	3.89	59
(c) 4 days	0.41	0.34	59.55	0.76	0.25	0.75	4.82	56
(d) 10 days	1.01	0.29	57.64	0.96	0.50	1.10	6.55	89

* ammonia increased after 10 days before centrifuging

TABLE II: STORAGE OF TJIR 1 CONCENTRATE

Age of concentrate when tested (days)	*Concentrate 1 (a)*				*Concentrate 1 (b)*				*Concentrate 1 (c)*			
	VFA No.	*KOH No.*	*Specific conductivity (mhos × 10³)*	*Mechanical stability (seconds)*	*VFA No.*	*KOH No.*	*Specific conductivity (mhos × 10³)*	*Mechanical stability (seconds)*	*VFA No.*	*KOH No.*	*Specific conductivity mhos × 10³*	*Mechanical stability (seconds)*
0	0.02	0.34	3.55	65	0.21	0.71	4.87	68	0.53	1.24	6.87	53
7	0.02	0.46	3.84	171	0.22	0.74	5.27	138	0.56	1.28	6.87	33
14	0.04	0.50	3.81	260	0.22	0.79	4.92	175	0.51	1.30	6.76	27
21	0.03	0.51	3.92	371	0.21	0.84	5.22	202	0.46	1.33	6.40	29
28	0.03	0.56	3.74	473	0.20	0.88	5.41	188	0.56	1.49	7.04	30
60	0.04	0.56	3.71	785	0.22	0.94	5.55	187	0.52	1.38	7.16	36
90	0.03	0.62	4.07	1,309	0.20	0.94	5.78	228	0.50	1.39	7.54	50
120	0.04	0.64	4.76	1,770	0.20	1.00	5.51	253	0.48	1.52	6.72	66
150	0.04	0.66	4.71	2,018	0.18	0.98	5.94	225	*Latex flocculated*			
180	0.04	0.72	4.46	2,453	0.23	1.04	6.08	332				

Age of concentrate when tested (days)	*Concentrate 2 (a)*				*Concentrate 2 (b)*			
	VFA No.	*KOH No.*	*Sp. cond. (mhos × 10³)*	*M. s. (sec)*	*VFA No.*	*KOH No.*	*Sp. cond. (mhos × 10³)*	*M. s. (sec)*
0	0.02	0.37	3.27	63	0.12	0.52	3.89	59
7	0.02	0.46	3.53	328	0.11	0.64	4.07	462
14	0.03	0.51	3.65	1,015	0.12	0.64	4.03	863
21	0.03	0.50	3.34	1,125	0.13	0.64	4.28	1,025
28	0.04	0.51	3.62	1,316	0.12	0.62	3.88	1,156
60	0.02	0.52	3.81	1,403	0.11	0.62	4.40	1,051
90	0.03	0.56	4.10	1,549	0.12	0.69	4.51	1,076
120	0.02	0.57	4.22	1,737	0.10	0.69	4.66	1,417
150	0.02	0.65	4.28	1,964	0.12	0.82	4.67	1,295
180	0.03	0.71	4.21	2,016	0.12	0.76	4.63	1,194

Sp. cond. = Specific conductivity

The main effect of the presence of volatile acids on mechanical stability was the prevention of increase on storage. This was very marked with the Tjir 1 concentrate when with a VFA No. of 0.02 the mechanical stability reached a value of over 2,000 seconds after six months, whereas with a VFA No. of 0.21 the mechanical stability remained constant after three weeks at values about 300 seconds.

Philpott and Sekar[9] state that the volatile acids consist mainly of acetic acid which is present in the latex serum as ammonium acetate. They have shown that mechanical stability was depressed by the addition of ammonium acetate. The effects of adding varying amounts of a 20% solution of ammonium acetate to six months old concentrate (see TABLES I and III 2(*a*)) are shown in *Figure 3*.

The increase in the mechanical stability on storage is usually attributed to the slow formation of long chain fatty acid ammonium soaps, which probably account in part for the slow increase in KOH No. on storage. When a latex has a high VFA content at the outset the slow formation of the long chain acid soaps still occurs, see TABLES II and III, but their normal effect upon the mechanical stability is negatived by the presence of the VFA anions. It is suggested that this depressant effect upon stability is the result of the increase in ionic strength which accompanies high VFA content, see TABLE I. This increased ionic strength

Concentrate 2 (c)				*Concentrate 2 (d)*			
VFA No.	*KOH No.*	*Sp. cond. (mhos × 10³)*	*M. s. (sec)*	*VFA No.*	*KOH No.*	*Sp. cond. (mhos × 10³)*	*M. s. (sec)*
0.25	0.75	4.82	56	0.50	1.10	6.55	89
0.21	0.84	4.97	318	0.50	1.23	6.12	271
0.23	0.81	4.71	685	0.50	1.15	6.65	382
0.23	0.80	5.24	766	0.49	1.12	6.35	424
0.22	0.80	4.94	791	0.49	1.15	6.88	437
0.20	0.81	5.41	811	0.46	1.17	6.35	429
0.21	0.93	5.49	744	0.47	1.26	7.03	409
0.22	0.88	5.69	992	0.45	1.28	6.81	463
0.23	0.97	5.37	956	0.46	1.28	6.67	454
0.24	0.93	5.37	1,058	0.48	1.31	6.55	433

M.s. = Mechanical stability

results in increased electrical conductivity, but a high conductivity in a given latex is not solely caused by a high VFA content because the conductivity of a fully preserved latex increases on storage even when the VFA remains unaltered.

VOLATILE ACIDS AND CONDUCTIVITY

STAMBERGER[13] has suggested that the rate of degradation in latex can be traced by conductivity determinations and MURPHY[3] and PATON[2] have shown that specific conductivity has a linear relationship with KOH No. It will be seen from TABLES II and III that specific conductivity increases both with the VFA No. and the KOH No. of latex concentrate. MADGE[4] suggests that long chain ammonium soaps contribute more to the KOH No. than to conductivity and it seems likely therefore that there may be a direct relationship between VFA No. and conductivity in freshly ammoniated field latex, where the long chain soaps have not usually been formed to any great extent.

Three latices from different sources were ammoniated to about 0.35% NH_3 and stored in stoppered demijohn bottles and in loosely covered buckets. Specific conductivities and VFA Nos. were determined at approximately the same time each day for a week and the results are plotted in *Figure 4*. Statistical examination indicates a significant linear relationship between specific conductivity $\times 10^3$ (y) and VFA No. (x) and a regression equa-

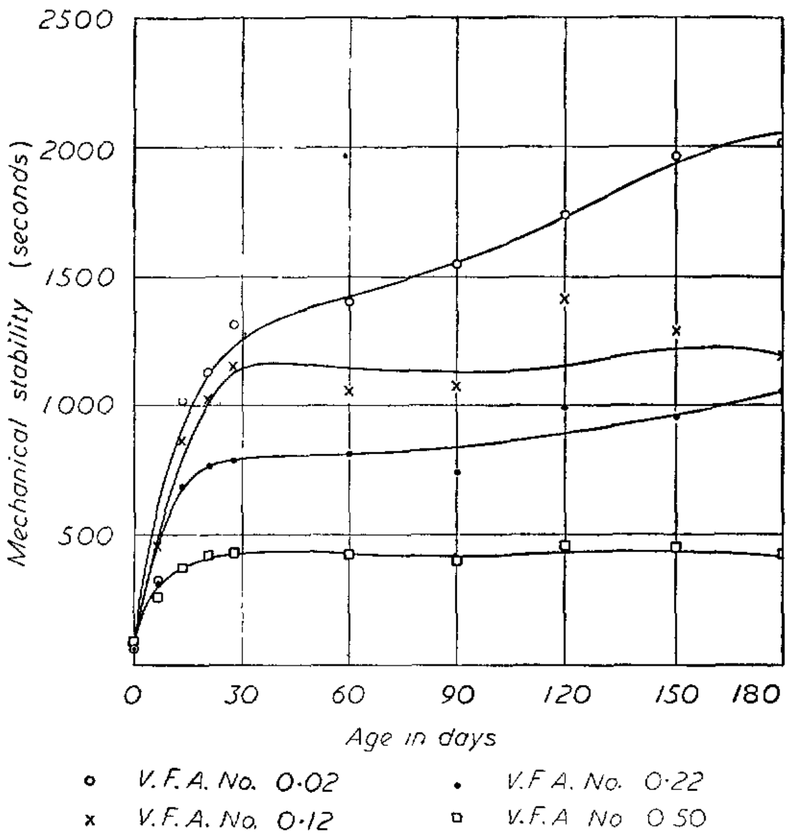

Figure 2. Increase in mechanical stability upon storage of concentrates made from mixed clonal and seedling latex at four levels of VFA No.

tion for the data is $y = 4.50 + 4.7x$, but an insufficient number of latices have been examined to justify adoption of this equation as a general rule. In practice a field latex conductivity exceeding 5×10^{-3} mhos indicates a VFA No. above 0.1.

The measurement of specific conductivity is quicker than the usual method for determining volatile acids, and might prove to be a useful method for factory control when many bulks of field latex have to be rapidly tested for quality.

DEVELOPMENT OF VOLATILE ACIDS

Since the formation of volatile acids in latex is mainly due to the action of micro-organisms[9], the quality of concentrate should depend largely on inhibition of contaminating bacteria by adequate preservation of the field latex. The following factors have been investigated:

AMMONIA CONTENT—Four gallon samples of mixed seedling and clonal latex were ammoniated to 0.2, 0.3, 0.4 and 0.5% NH_3 and stored in buckets with loose covers. VFA Nos. were determined each afternoon until values of about 0.5 were reached.

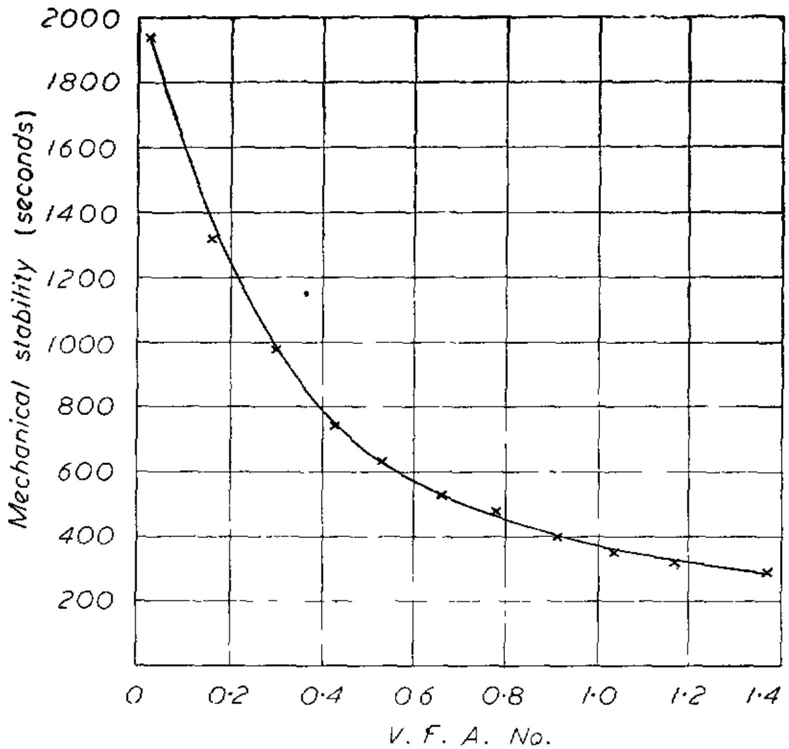

Figure 3. Effect of addition of ammonium acetate upon the mechanical stability of a well preserved concentrate.

The development of volatile acids with age of the latex is shown in *Figure 5*. The curves show that the formation of volatile acids is delayed for a certain time depending on the amount of ammonia present, thereafter they increase rapidly and this rapid increase usually takes place after a value of 0.1 is reached.

USE OF FORMALDEHYDE—Similar samples of latex to the above were treated with 0.05% formaldehyde one hour before ammoniating to 0.15, 0.2 and 0.3% NH_3. The development of volatile acids is compared in *Figure 6* with development in latex containing 0.3% NH_3 only. The addition of formaldehyde delayed the production of volatile acids for longer periods than did comparable quantities of ammonia alone. Centrifuged concentrate prepared from three days old field latex treated with formaldehyde and ammonia compared favourably in properties with concentrate prepared from fresh field latex containing 0.3% NH_3. The addition of 0.05% formaldehyde to 0.3% ammoniated field latex immediately upon receipt at the factory was equally effective in delaying the onset of volatile acid formation.

TIME OF AMMONIATION—Philpott and Sekar[9] have shown that volatile acids develop rapidly in fresh field latex. The time of ammoniation, therefore, should have an important bearing on the quality of the concentrate produced. Samples of mixed clonal

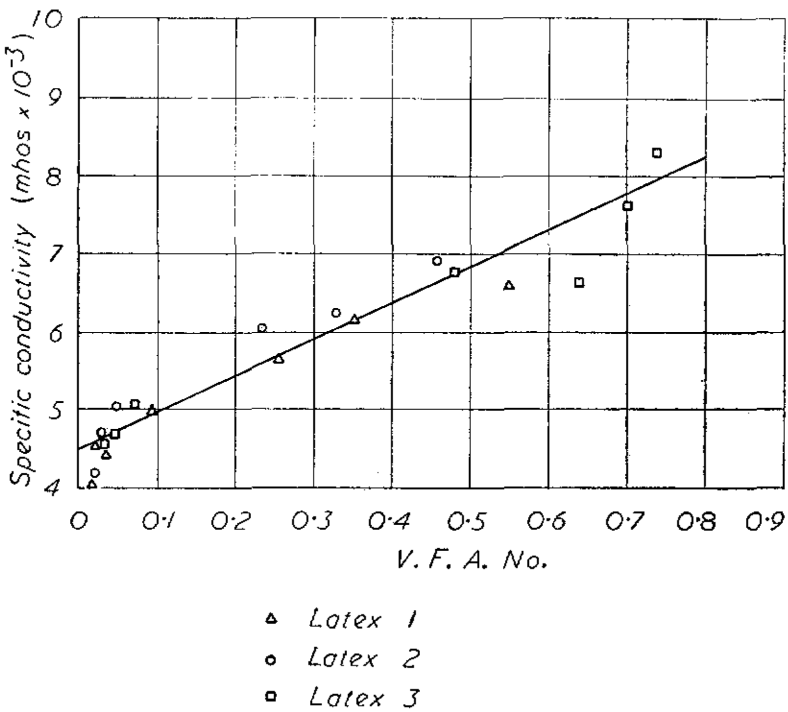

Figure 4. The correlation between electrical conductivity and VFA No.

and seedling latex were ammoniated to 0.3% NH_3 at 12 noon, 2 p.m., 3 p.m., 4 p.m., and 5 p.m. The increase in VFA No. on storage is shown in *Figure 7*. Delay in ammoniating caused an increase in the VFA No. of the field latex which would be reflected in a higher VFA No. in the concentrate.

MIXING OLD AND NEW FIELD LATEX—It is sometimes a practice in latex factories not to centrifuge all of each day's latex within twentyfour hours of collection but to mix freshly collected latex with some of the old material. To find the effect of this practice on the VFA No. of concentrate, 90 gallons of mixed seedling and clonal latex were collected and ammoniated to 0.3% NH_3 before noon. Sixty gallons were centrifuged during the next morning and another 60 gallons of freshly ammoniated latex mixed with the residual 30 gallons. This procedure was repeated for seven days. VFA Nos. were determined immediately before and after centrifuging and are plotted in *Figure 8*. It is evident that mixing of old and new field latex has a cumulative effect on the VFA No. and the quality of the concentrate.

RELATION BETWEEN VFA NO. OF FIELD LATEX, CONCENTRATE AND SKIM

Since the VFA No. of well preserved centrifuged concentrate remained sensibly constant during six months storage, it would

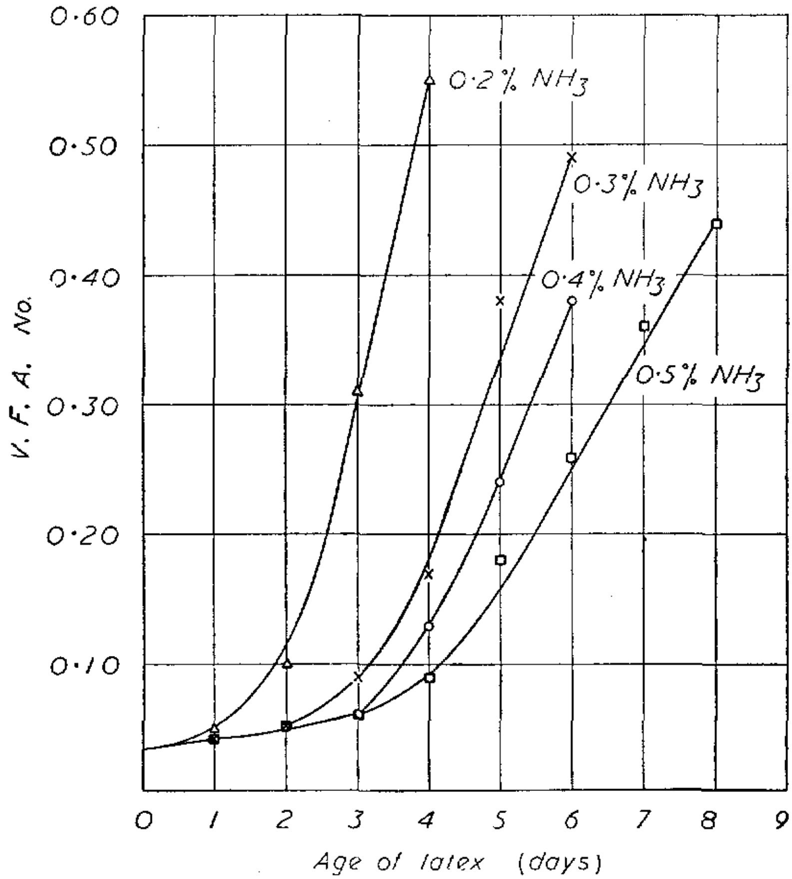

Figure 5. Effect of different levels of ammoniation on the increase in VFA No.

appear that the amount of volatile acids in the concentrate depended directly on the amount of volatile acids in the ammoniated field latex. Theoretically, the VFA No. of a 60% d.r.c. concentrate should be about one third to one half of the VFA No. of a 35% d.r.c. field latex, depending on the total solids content of the latex and assuming that the volatile acids are present in the serum. To investigate this, three different types of latex were collected, ammoniated to 0.3% NH_3 and centrifuged after varying time intervals.

The VFA Nos. were determined on the ammoniated field latex and on the concentrate and the skim after centrifuging. The results are given in TABLE IV and the VFA No. are compared by expressing the volatile acids as gm KOH per 100 gm serum which is taken as 100-d.r.c. The concentration of volatile acids in the serum of the field latex does not differ significantly from that of the serum of the concentrate, suggesting that volatile acids are not associated with the rubber phase. The concentration

TABLE IV: RELATION BETWEEN VFA NO. OF FIELD LATEX, CONCENTRATE AND SKIM

Type of latex	*Field latex*			*Concentrate*			*Skim*			*Volatile acids expressed as gm KOH per 100 gm serum (i.e. 100 - d.r.c.)*		
	t.s. (%*wt*)	*d.r.c.* (%*wt*)	*VFA No.* (*gm KOH 100 gm t.s.*)	*t.s.* (%*wt*)	*d.r.c.* (%*wt*)	*VFA No.* (*gm KOH 100gm t.s.*)	*t.s.* (%*wt*)	*d.r.c.* (%*wt*)	*VFA No.* (*gm KOH 100 gm t.s.*)	*Field latex*	*Concentrate*	*Skim*
Mixed clonal and seedling latex from RRI Expt. Station	39.82	36.38	0.056	57.82	55.62	0.025	14.11	9.14	0.142	0.035	0.033	0.022
	39.82	36.38	0.341	64.30	62.41	0.121	15.56	10.12	0.736	0.213	0.207	0.128
	39.82	36.38	0.535	57.54	54.62	0.300	15.63	9.76	1.89	0.335	0.380	0.328
Mixed seedling latex from Ulu Klang smallholding	37.05	34.12	0.293	66.09	65.08	0.085	23.55	20.62	0.470	0.165	0.161	0.139
	37.56	34.69	0.352	63.70	62.22	0.118	13.68	10.44	1.050	0.202	0.199	0.160
	35.24	32.24	0.509	65.40	63.78	0.172	16.46	12.99	1.592	0.265	0.311	0.301
Tjir 1 latex from Field 31 at RRI Expt. Station	49.62	46.47	0.256	64.52	62.46	0.159	30.19	27.07	0.606	0.237	0.273	0.251
	47.68	44.42	0.353	64.12	62.10	0.161	25.74	21.65	0.758	0.303	0.272	0.249
	47.35	44.38	0.586	59.41	57.20	0.382	19.13	15.26	2.57	0.499	0.530	0.580

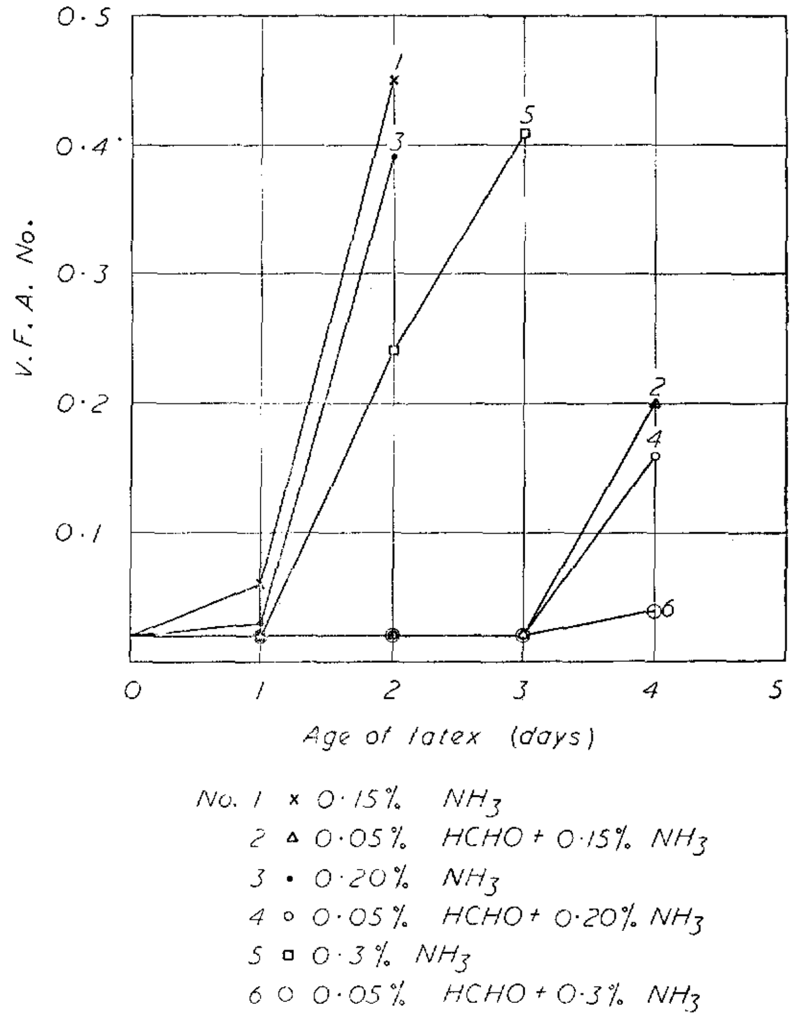

Figure 6. Addition of formaldehyde delays the rise in VFA No. for several days.

of volatile acids in the concentrate is significantly greater than that in the serum of the skim. Moreover, this difference between concentrate and skim increases with increasing volatile acid content. This indicates that some volatile acids are removed in the sludge during centrifuging.

PURIFYING LOW GRADE CONCENTRATE

As the volatile acids are present mainly in the serum, they can be removed by dilution and reconcentration of the latex. TABLE V shows the improvement obtained by diluting a poor quality concentrate with water to approximately 35% d.r.c. and recentrifuging.

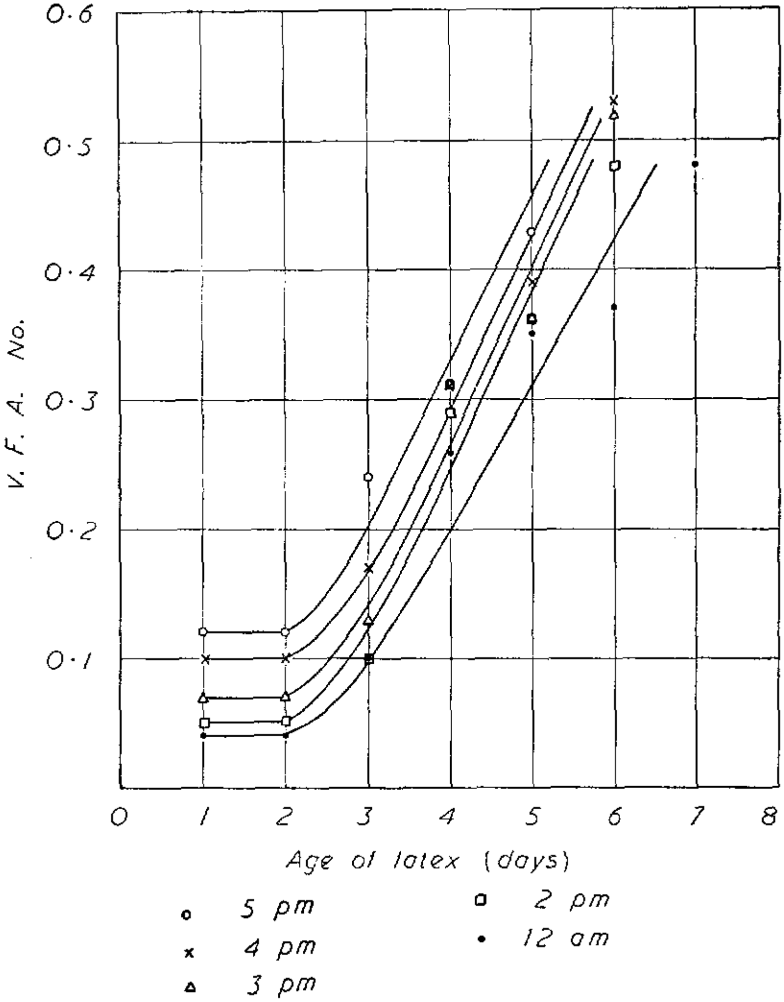

Figure 7. Effect of delay in ammoniation upon the increase in VFA No.

DISCUSSION

Volatile acids in centrifuged latex concentrate have been shown to affect considerably the mechanical stability. Volatile acids develop rapidly in the field latex before centrifuging and since their formation is attributed to contaminating micro-organisms, the first essential for the production of high quality concentrate is cleanliness at all stages of preparation. The acids are produced in fresh latex and ammoniation at an adequate level should take place as soon as possible after tapping. A small quantity of formaldehyde followed by less than the normal amount of ammonia appeared to give good preservation of field latex. After a few days, volatile acids develop rapidly in latex ammoniated

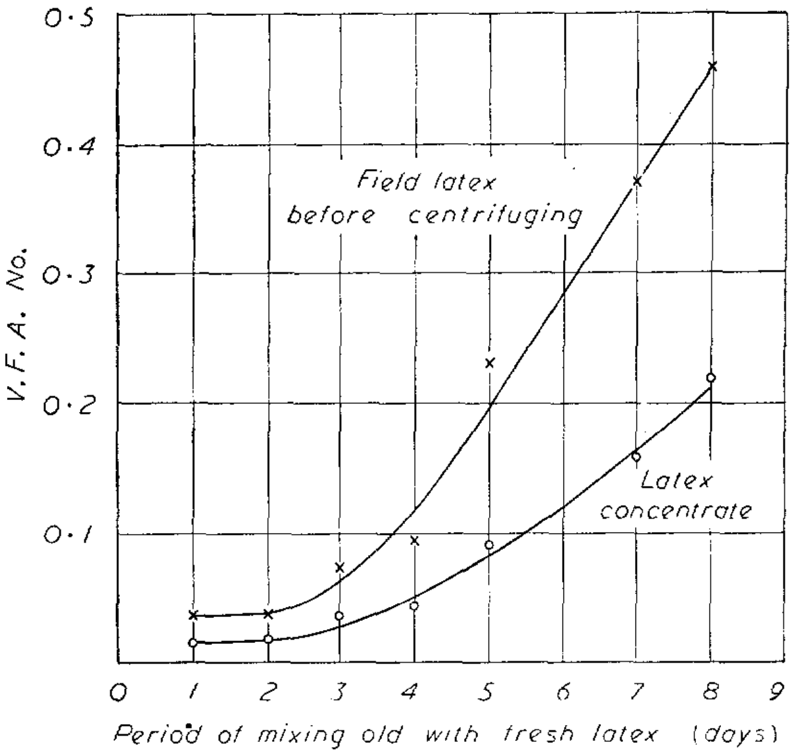

***Figure 8.* Effect upon VFA No. of adding some of the previous days crop.**

TABLE V: RECENTRIFUGING LOW GRADE CONCENTRATE

Test	*Centrifuged concentrate*	*Re-centrifuged concentrate after diluting with water*
d.r.c. (%wt)	57.76	63.87
Total solids (%wt)	59.63	64.63
Ammonia (%wt)	0.79	0.87
V.F.A. No.	0.18	0.07
KOH No.	0.71	0.34
Mechanical stability (seconds)	263	778
Odour after neutralisation with boric acid	*Slight putrefaction*	*Sweet*

to between 0.2 and 0.5% NH_3 and since between one third and one half of the VFA No. of the field latex is transmitted to the concentrate, it is advisable to centrifuge field latex soon after collection, preferably within twentyfour hours. Newly collected latex should not be mixed with old ammoniated field latex before centrifuging. Poor quality concentrate having a high VFA No. can be purified by diluting with water and recentrifuging.

In many instances specific conductivity may be used as a means of controlling the quality of incoming field latex to be processed as concentrate, since it is related to the VFA No.

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