

Viscosity of Latex Mixes Using a Full Two-level Factorial Design[†]

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Good viscosity stability of latex compounds is important for production processes. The effect of additions of potassium laurate, zinc oxide and ammonium sulphate on the viscosity of a natural rubber latex concentrate were investigated using a full two-level factorial design. The main and interaction effects were found to be large and significant as calculated by Yates Algorithm. Thus, all three variables jointly influenced the viscosity stability of latex compounds. When potassium laurate and ammonium sulphate were at the +1 levels, the increases in viscosity of the latex compounds were found to be large and gelation took place on overnight maturation. The destabilising effect of the laurate has been interpreted based on the results of radiotracer investigations on ¹⁴C-laurate soap adsorption on latex particles, which showed appreciable surface protein displacement by the added soap at high soap concentrations. A similar interpretation is made – albeit less conclusively – when the nitrogen values of the cream fraction of latex which was treated with high laurate concentrations were examined. Further, the destabilising influence of ammonium sulphate on latex compounds is discussed together with some data showing the relationship between ammonia/ammonium concentrations and zinc oxide solubility as measured by a ⁶⁵Zn-radiotracer method.

There are many factors which have been suggested or shown to affect the viscosity of a latex compound^{1,2}. These include solubility of zinc-containing compounds like zinc oxide and zinc dialkyldithiocarbamates, level and type of added stabilisers, inherent stability of raw latex concentrate and miscellaneous factors such as total solids content, storage conditions, temperature, latex types and preservation systems. Although a wealth of information is available on the effects of most of these factors, there exist gaps in these databases. One typical example is the conflicting reports on the effect of higher fatty acid soaps on zinc oxide thickening³⁻⁸. This lack of coherence may be due to the fact that previous workers have designed their experiments using the inferior method of varying one factor at a time while ostensibly holding other variables at constant levels.

There are many drawbacks of the one-factor-at-a-time method. They are comprehensively described in most textbooks on design of experiments^{9,10}. Of the disadvantages, two are of particular relevance to the work here. Firstly, the one-factor-at-a-time method does not make use of the experimental data as effectively as the statistical design of experiments – usually abbreviated as DOE. To obtain estimates of the main effects of three variables with the same precision as provided by a 2³ factorial design, for example, the one-factor-at-a-time method would require twenty-four runs – a three-fold increase. Of these runs, 20 degrees of freedom (DF) are associated with the error (unknown factors) and only 3 are associated with the factors. In a statistical sense, the more degrees of freedom associated with an item, the more information is known about the effect of this

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item. Based on this interpretation, the one-factor-at-a-time method is undoubtedly a very poor test strategy. In fact, what are the problems solved by knowing a lot about error? The factorial design actually trades the error DF for DF of the factors while maintaining orthogonality among the factors and interactions. Secondly, the one-factor-at-a-time experiments are particularly sensitive to the presence of interaction. If interactions are present, the magnitude and directions of the effect estimates produced by a one-factor-at-a-time experiment may be so misleading that extremely poor results are obtained when these effect estimates are interpreted jointly. This problem is easily overcome by factorial design which detects and evaluates interactions clearly.

This paper discusses results of recent experiments using a full two-level factorial design to study the effects of additions of potassium laurate, ammonium sulphate, and zinc oxide on the viscosity changes of a natural rubber latex concentrate. Wherever possible, attempts are made to explain the chemistry of the main and interaction effects observed using the results of present investigations together with some published information.

EXPERIMENTAL

Materials

Latex concentrates. For the factorial and soap adsorption experiments, the latex used was a high-ammonia (HA) centrifuged natural rubber latex concentrate which had been matured for more than four months. The properties of this matured latex conformed to the ISO 2004:1979 specifications.

For experiments on zinc oxide solubility, three latex concentrate samples were used. The first sample was a low-ammonia, TMTD:zinc oxide preserved latex concentrate with 0.20% NH_3 and 0.74 KOH No. (labelled as LA-TZ A). This was then diluted to 40% TSC and recentrifuged. The resultant latex was then topped up with ammonia to become reprocessed HA latex

concentrate (the second sample), and with TZ and ammonia to become reprocessed LA-TZ latex concentrate (the third sample), labelled as LA-TZ B.

Chemicals. Potassium laurate soap of 20% strength was prepared by saponification of lauric acid (Sigma Grade of 99% – 100% purity) with stoichiometric amounts of potassium hydroxide of 85% purity obtained from Merck.

Zinc oxide was added to latex as an approximately 50% dispersion in water. It was prepared by ballmilling a mixture comprising 100 parts by weight of zinc oxide, 98 parts of water, and 2 parts of a polyethylene oxide condensate (Vulcastab LW) for 24 h.

The ammonium sulphate used was obtained from Fluka Chemical Company and had a purity greater than 99.5%.

Wherever possible, all the other materials used in this work were of analytical reagent grade.

Radiotracer. For measurements of zinc oxide solubility, ^{65}ZnO purchased from Unit Tenaga Nuklear, PUSPATI, Bangi was used. In the case of the experiments on laurate soap adsorption, the radiotracer used was a ^{14}C -labelled lauric acid of code: CFA 106 from Radiochemical Centre, Amersham, England.

Factorial Experiments

Preparation of the mixes. Potassium laurate, zinc oxide and ammonium sulphate were added to the latex in two parts. *Part I* comprised ammonium sulphate and zinc oxide dispersion and this was added to *Part II* which was made up of latex, soap and a calculated amount of water to adjust the total solids content of the mix to 55%. The amounts of ingredients added to the latex are shown in the design matrix of *Table 1*.

In accordance with the basic principles of DOE¹⁰, the order of the runs was randomised and experiments duplicated.

TABLE 1. TWO-LEVEL FACTORIAL EXPERIMENTAL DESIGN

Run No.	Potassium laurate (A)	Ammonium sulphate (B)	ZnO (C)
1	-1	-1	-1
2	+1	-1	-1
3	-1	+1	-1
4	+1	+1	-1
5	-1	-1	+1
6	+1	-1	+1
7	-1	+1	+1
8	+1	+1	+1

-1 and +1 indicate the low and high levels of the additive

Potassium laurate, -1: 0.15 p.h.r., +1: 0.74 p.h.r.

Ammonium sulphate, -1: 0.1 p.h.r., +1: 1 p.h.r.

ZnO, -1: 0.5 p.h.r., +1: 5 p.h.r.

Viscosity measurements. The viscosities of the latex mixes were measured after the specified time periods using a Brookfield viscometer (model LVF) with spindle No. 2 at 60 r.p.m. and 25°C.

Radiotracer Experiments

⁶⁵Zn assay. The radioactivity in the form of gamma radiation emitted from ⁶⁵Zn was

assayed using the Cobra One 5003 Auto Gamma from Packard, USA. The counting window was centred around 1120 KeV, the annihilation peak of the positron (*Figure 1*). The solubility of zinc oxide (⁶⁵ZnO) in the latex serum was calculated using the equation:

$$^{65}\text{ZnO} = (A_s/mA_{sp}) * 100$$

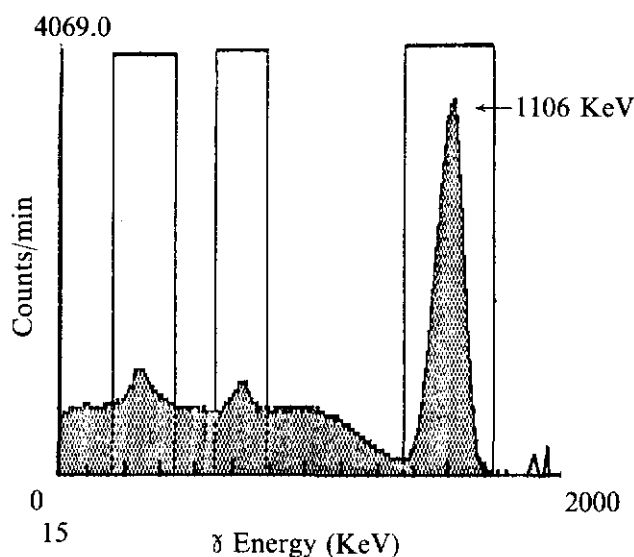


Figure 1. Gamma spectrum of ⁶⁵ZnO.

where A_s : activity of the saturated solution

m : weight of the saturated solution

A_{sp} : specific activity of solid ZnO.

Soap adsorption. The method used has been described elsewhere^{11,12}. It was based on liquid scintillation counting of ^{14}C -radioactivity using the Beckman LS9000 counter.

Nitrogen Determinations

Nitrogen contents of the cream fraction of latex samples obtained by ultracentrifugation were determined by the Kjeldahl method¹³. Centrifugation was carried out at 25 000 r.p.m. for 45 min on rotor 40 in the Beckman L8-70 ultracentrifuge.

Atomic Absorption Spectrophotometry

Analysis of zinc in latex serum was carried out by first ashing the dried serum for 4 h at 550°C, followed by the standard digestion procedure as described in the laboratory manual¹³. The digest was then assayed for zinc using a Varian Techtron AA5 Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSIONS

The mean Brookfield viscosity values of the runs as described in the design matrix of Table 1 are diagrammatically represented at the corners of the cube in Figure 2. The results of factorial analysis which show the calculated effects of the factors after 1 h of storage of the latex mixes and the standard errors are collected in Table 2. The standard error of an effect, $s/2$ is calculated using the

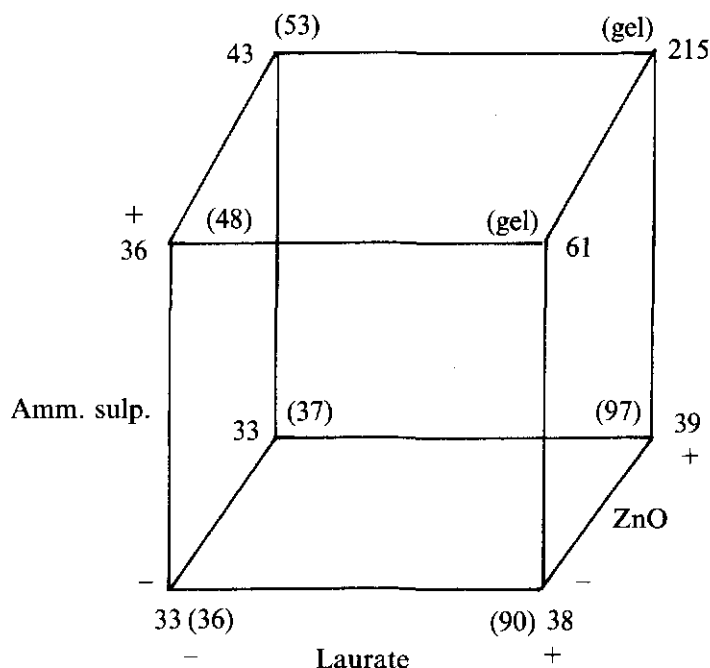


Figure 2. Two-level factorial design with viscosity data displayed geometrically. (Figures within brackets : viscosity after 24 h maturation; Others figures : viscosity after 1 h storage.)

TABLE 2. CALCULATED EFFECTS AND STANDARD ERRORS FOR THE 2³ FACTORIAL DESIGN

Variable	Effect viscosity (1 h)	Std. error
Mean	62	1.3
A	52	2.6
B	53	2.6
AB	47	2.6
C	41	2.6
AC	37	2.6
BC	40	2.6
ABC	37	2.6

formula⁹: $s^2 = \Sigma (d_i^2)/2g$ where d_i is the difference of the duplicate observations for the i^{th} set of conditions and g is the number of sets of combinations of the design which is equal to 8. The standard error of the mean is given by $s/N^{0.5}$ where N is the total number of runs.

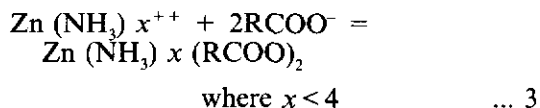
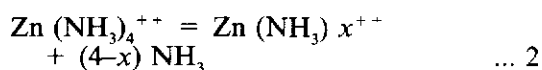
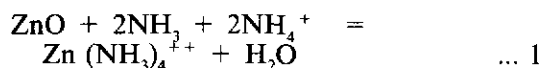
It is evident from *Table 2* that the main and interaction effects as calculated by Yates Algorithm are large and significant when compared to the standard errors. In view of this, the main effects cannot be interpreted individually and are therefore considered jointly in the following sections.

Effect of Addition of Zinc Oxide

Table 3 shows that increasing zinc oxide concentrations from 0.5 p.h.r. to 5 p.h.r. did

not cause appreciable increases in viscosity except for the recipe that contained high concentrations of potassium laurate and ammonium sulphate. This clearly demonstrates that zinc oxide by itself did not cause latex thickening, but it was the interaction of zinc oxide with ammonium ion and laurate soap that brought about the viscosity increase.

The interactions may be depicted by the following stoichiometric equations¹⁴:



The dependence of zinc oxide solubility on ammonia, and ammonium ion concentrations (*Equation 1*) was examined by a ⁶⁵Zn-radiotracer technique. Results obtained (*Table 4*) show that at a constant ammonia concentration of 0.2%, a decrease of 0.36 units in KOH No. resulted in a decrease of 0.16% in zinc oxide solubility. The solubility of zinc oxide in the HA latex of 0.81% ammonia and 0.30 KOH No. was 0.29% higher than the LA-TZ latex which had a KOH No. of 0.38. It is evident therefore that zinc oxide solubility in latex is dependent on ammonia and KOH No. which is a concentration measure of am-

TABLE 3. EFFECT OF ADDITION OF ZINC OXIDE ON VISCOSITY OF LATEX MIXES

Effect of increasing ZnO from 0.5 p.h.r. to 5 p.h.r.		Condition at which comparison is made	
Changes in viscosity		Laurate	Amm. sulph.
1 h	24 h	(p.h.r.)	(p.h.r.)
0	1	0.15	0.1
1	7	0.74	0.1
7	5	0.15	1
154	Gel	0.74	1
Main effect = 41		All the above conditions	

TABLE 4. EFFECT OF AMMONIA CONCENTRATION AND KOH NO. ON ZINC OXIDE SOLUBILITY

Sample	NH ₃	KOH No.	pH	S _{ZnO} (% wt)
LA-TZ (A)	0.20	0.74	9.58	0.22 ^a ; 0.23 ^b
LA-TZ (B)	0.19	0.38	9.89	0.06 ^a ; 0.06 ^b
HA	0.81	0.30	10.75	0.35 ^a ; 0.36 ^b

^aBy radiotracer method^bBy atomic absorption spectrophotometric method

monium forms of acid anions in latex. pH values are also included in the table to monitor the changes in acidity of the latex due to the variations in KOH No. and ammonia.

Regarding *Equations 2 and 3*, the number of ligands complexed with zinc varies from one to four. The various ammine complexes are all in equilibrium with each other and with the non-ammoniated zinc ions. Notwithstanding the recent proposal¹⁵ that latex destabilisation is caused by an increase in the amount of all the dissolved zinc ions, the general opinion is that it is the lower zinc amines ($x < 4$) rather than the higher ones (e.g. $x = 4$) that are responsible for the destabilisation. When complexed with carboxylate soap, the zinc ammine ions form insoluble zinc soap. This leads to a reduction in electrical double layer repulsion among latex particles, which subsequently results in a decrease in latex stability and an increase in viscosity.

Effect of Addition of Ammonium Sulphate

The effect of increasing ammonium sulphate concentration from 0.1 p.h.r. to 1 p.h.r. on the viscosity of the latex mixes was much dependent on the level of added laurate soap (*Table 5*). At low soap concentration, the effect was small, but at high soap concentration, the effect was greater especially on overnight maturation. Gelation of the compound was observed when it was stored overnight at ambient temperature.

Comparison of the figures in the second and fourth rows of *Table 5* shows that the viscosity increase after 1 h of maturation as effected by increasing ammonium sulphate concentration was also dependent on the level of the added zinc oxide, reflecting the presence of strong interaction among the three additives.

TABLE 5. EFFECT OF ADDITION OF AMMONIUM SULPHATE ON VISCOSITY OF LATEX MIXES

Effect of increasing ammonium sulphate from 0.1 p.h.r. to 1 p.h.r.		Condition at which comparison is made	
Changes in viscosity		Laurate	ZnO
1 h	24 h	(p.h.r.)	(p.h.r.)
3	12	0.15	0.5
23	Gel	0.74	0.5
10	16	0.15	5
176	Gel	0.74	5
Main effect = 53		All the above conditions	

TABLE 6. EFFECT OF ADDITION OF LAURATE SOAP ON VISCOSITY OF LATEX MIXES

Effect of increasing laurate from 0.15 p.h.r. to 0.74 p.h.r.		Condition at which comparison is made	
Changes in viscosity		Amm. sulph.	ZnO
1 h	24 h	(p.h.r.)	(p.h.r.)
5	54	0.1	0.5
25	Gel	1	0.5
6	60	0.1	5
172	Gel	1	5
Main effect = 52		All the above conditions	

Effect of Addition of Potassium Laurate Soap

Table 6 shows that when ammonium sulphate concentration was low, the viscosity increase due to increasing potassium laurate soap concentration was small after 1 h of storage but became ten times larger on overnight maturation. This shows that destabilisation of the compounded latex is a time-dependent process. Blackley⁸ has also observed a similar effect on the heat sensitivity of his compounded latex. He explained the increase in heat sensitivity with maturation time by invoking the assumption that the displacement of macromolecules by carboxylate soaps was a very

slow process. However, this assumption appears to be at variance with the results of Figure 3 which show that the adsorption isotherms of laurate soap on latex particles were unaffected by equilibration times over a wide range of laurate soap concentrations. In other words, adsorption of laurate soap on latex particles appeared to be a fast process even at high soap concentration when proteins were expected to be displaced.

The question of how exactly maturation time affects latex compound viscosity, therefore, remains unresolved but is an interesting topic for further investigations.

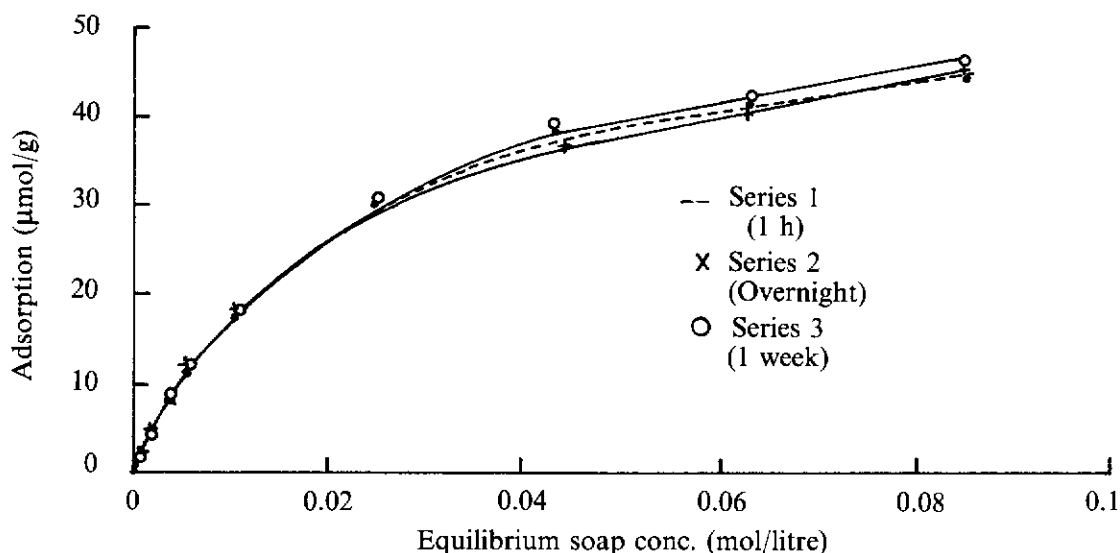


Figure 3. Effect of equilibration time on laurate soap adsorption.

With ammonium sulphate at the +1 level, increasing potassium laurate soap concentration from 0.15 p.h.r. to 0.74 p.h.r. effected a sharp rise in latex viscosity after 1 h of maturation (*i.e.* a large increase in viscosity values); on overnight maturation, the compounds gelled. While it is well-known that ammonium sulphate can destabilise latex by sensitising the dissolution of zinc oxide through a non-specific screening effect¹⁶ where the thickness of the diffuse double layer is reduced to the point where Van der Waals attraction dominates the net potential energy of interaction, it would appear contradictory that potassium laurate soap which would normally be thought of as a stabiliser actually destabilises latex in the presence of zinc ammine ions. To reconcile this paradox, it is necessary to draw on the hypothesis of surface protein displacement by the adsorbed laurate soap and support it with results of recent investigations.

Surface Protein Displacement

In discussing possible explanations for the destabilising effect of potassium laurate soap on compounded latex in the presence of zinc ammine ions, it may be appropriate to mention, first of all, the findings of Lai and Chen¹² who studied the adsorption isotherms of laurate soap on NR latex particles using ¹⁴C-radiotracer technique. In outline, they have provided experimental evidence (*Figure 4*) which indicated that displacement of surface proteins began to take place when added laurate soap concentration exceeded about 0.4 p.h.r. (equivalent to equilibrium soap concentration of 0.008M when *Curve D* began to decline), and that further addition of laurate soap led to considerable displacement of proteins. At high soap concentrations, therefore, the latex would be covered and stabilised mainly by the added soap. Since interaction between

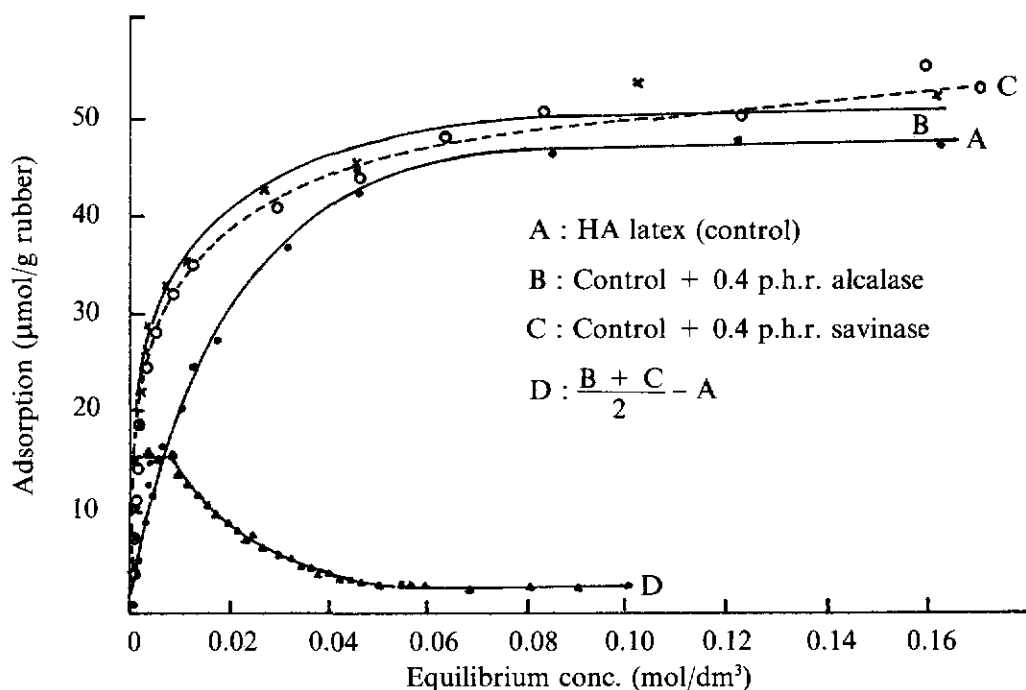


Figure 4. Effect of enzyme treatment on laurate soap adsorption at 25°C.

zinc ammine ions and soap forms insoluble zinc soap, the latex mix will be destabilised through loss of charge. But, at low soap concentrations, the latex mix is stabilised by the interfacial macromolecular species like the proteins which are expected to be less sensitive to zinc ion destabilisation. It is not surprising therefore that laurate soap, when added at high concentrations, actually leads to gelation of the latex in the presence of zinc oxide on overnight maturation at ambient temperature.

To confirm the findings of Lai and Chen¹², the nitrogen contents of the cream fractions of three latex concentrate samples which have been treated with 1 p.h.r., 1.5 p.h.r. and 2 p.h.r. of potassium laurate were compared with those of the control latices. It is evident from Table 7 that large additions of laurate soap had effected decreases in cream nitrogen values: they were 35%–41% lower than those of the control. As nitrogen content is related to the protein level, these figures may be interpreted as an indication that the bulk of the surface proteins was not displaced into the serum phase by the added laurate soap. At first glance, this conclusion seems to be in conflict with that reported in the preceding paragraph. However, by considering the following experimental details and possibilities:

- i) The cream nitrogen values were obtained after one centrifugal run; it is unlikely therefore that the proteins which have been displaced from the particle surface can be efficiently separated from the cream fraction of the latex. Some of the displaced

proteins may be entrapped in the cream fraction and are not released into the serum phase during centrifugation.

- ii) Under the conditions of the experiments, 14% by weight of the cream was actually latex serum.
- iii) It is possible that the displaced proteins are re-adsorbed onto the surface of the soap micelle¹⁷ resulting in a net increase in effective diameter of the micelle. With this increase, the micelle-protein aggregate would be expected to move upwards and become inseparable from the cream fraction on ultra-centrifugation since larger particles of density lower than that of the continuous phase cream faster than the smaller ones in a centrifugal field (corollary of Stokes law).

It is apparent that the actual surface nitrogen concentrations were considerably lower than the cream nitrogen values for latices which had been treated with high laurate soap concentrations. In other words, large additions of laurate soap had actually effected decreases in surface nitrogen level significantly greater than 40%. Although it is not possible to estimate the actual level of protein displacement quantitatively using this approach, it would not be too unreasonable to suggest (based on the above information) that at high soap concentrations, displacement of proteins from the latex particle surface was appreciable.

SUMMARY AND CONCLUSIONS

A full two-level (2³) factorial design has been successfully used to study the effect

TABLE 7. NITROGEN CONTENTS OF THE CREAM FRACTIONS OF LATEX CONCENTRATES

Latex	Cream (%)	Drop in N (%)
Control (Ctrl)	0.17	
Ctrl + 1 p.h.r. KL	0.11	35.3
Ctrl + 1.5 p.h.r. KL	0.10	41.2
Ctrl + 2.0 p.h.r. KL	0.10	41.2

KL : Potassium laurate

of addition of potassium laurate soap, zinc oxide and ammonium sulphate on the viscosity of a natural rubber latex concentrate. In contrast with previous work done in this field, the factorial experiments have unambiguously identified and estimated the interaction effects of the above-mentioned factors on the viscosity of the latex mixes.

Other salient points presented and discussed include:

- The fast rate of adsorption of laurate soap on latex particles and its conjectural displacement of surface proteins.
- Experimental evidence for the above adsorption-displacement conjecture.
- Measurement of zinc oxide solubility by ^{65}Zn -radiotracer method.

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