OBSERVATIONS ON THE COAGULATION OF HEVEA LATEX.

BY

R. G. FULLERTON.

INTRODUCTION.

A great deal of attention has been given to a study of coagulation phenomena in rubber latex, but, until recently, investigations have been hampered by the absence of a satisfactory method for the accurate definition of the various stages in the coagulation process in terms of the hydrogen ion concentration of the medium. Among the first to draw attention to the importance of establishing satisfactory methods for the measurement of hydrogen ion concentration was Belgrave (1) who made use of the hydrogen electrode and compared the results of electrometric measurements with those obtained colorimetrically by means of indicators. He found that results obtained electrometrically in this way were uncertain owing to coagulation of the latex on the platinised hydrogen electrode, and with indicators it is difficult to make colorimetric comparisons when working with a cloudy liquid. More recently, however, van Harpen (2) and van Dillen (3), have made use of the quinhydrone electrode to make more accurate observations of the various stages in the process. The present paper describes some observations which have been made with the aid of the quinhydrone electrode applied to the study of hydrogen ion concentration of latex under the influence of acids and certain preservatives.

TECHNIQUE.

The technique followed in the making of measurements and the assembly of the apparatus followed very closely that recommended by Biilmann and Tovborg-Jensen (4) for the determination of pH values in soil-water mixtures. In both electrodes the metallic electrode used was a piece of bright platinum foil, about 1 centimetre square, welded to a platinum wire fused into a glass tube. The standard electrode used was the quinhydrone electrode, the electrolyte of which was prepared by mixing 900 c.cs of $\frac{N}{10}$ KCl. with 100 c.cs of $\frac{N}{10}$ HCl. The potential was measured by means of the portable type of potentiometer supplied by the Cambridge Instrument Co., Ltd. Before making a series of determinations the apparatus was standardised by measuring the pH in a standard buffer solution of known composition. For this purpose an $\frac{M}{20}$ solution of potassium hydrogen phthalate was used, the pH of which is 3.97 between 20° and 30°C. The quinhydrone was prepared according to the methods recommended by Biilmann and Lund, (4) 0.1. g. of the solid being added per 25 c.c. of solution in either of the two electrode vessels.

For this system Biilmann has developed the equation:—

$$pH = 2.03 + \frac{\pi}{0.0001984 \times T}$$

where π is the measured potential in volts and T is the absolute temperature. He has shown that for a temperature fluctuation in the electrode of $\pm$ 1°C the error introduced is not greater than 0.05 of a unit of pH. Since room temperature in the tropics is fairly constant at 29° $\pm$ 1°C, a thermostat was not used in the experiments to be described. For each single measurement the temperature of the solution, whose pH was to be determined, was recorded and it was found that the average fluctuation about the value 29°C was 0.5°.

For determinations of the pH of latex in a state of flocculation or coagulation the pH values of the sera were obtained.

Before proceeding with the main investigation it was necessary to determine (a) whether there is an appreciable drift of potential in making a measurement with latex and (b) the accuracy with which results can be reproduced for the same latex within reasonable limits of time.

To determine the first point fresh undiluted latex and the same latex diluted to a low rubber content were examined. Two samples —A and B—from different groups of trees on the same estate were collected shortly after tapping. Diluted latices, in the proportion latex : water = 1 : 9, were prepared from each of the two original samples, and all four latices allowed to stand for about 15 minutes with occasional gentle stirring. Measurements were then taken in the order—sample A undiluted, sample A diluted, sample B undiluted, sample B diluted. For each series of measurements the procedure was as follows:—

Quinhydrone was added to a portion of the sample in a test-tube —about 0.1 g. per 25 c.c. latex—and the mixture stirred together for a few seconds with a glass rod. The test-tube with contents was then placed in position in the apparatus, which had previously been standardised and tested. A reading for E.M.F. was then taken as soon as possible and the time for this referred to as zero. Readings were then taken for the sample at definite intervals, usually 10 seconds, over a total period of about 10 minutes. The test-tube was then removed and the platinum electrode was cleaned by rinsing with distilled water and heating to redness. The apparatus was then standardised and made ready for the next series of measurements. The pH of all four samples was then determined after a period of four hours. Table I summarises the results obtained. It will be seen that the potential attains its maximum value almost immediately and there is, thereafter, a slight drift in the direction of decreasing

TABLE I.

DRIFT OF POTENTIAL WITH TIME.

LATEX SAMPLE A.				LATEX SAMPLE B.			
UNDILUTED		DILUTED 1: 9		UNDILUTED		DILUTED 1: 9	
Time in Secs.	pH.	Time in Secs.	pH.	Time in Secs.	pH.	Time in Secs.	pH.
0	6.80	0	6.48	0	6.81	0	6.42
10	,,	10	,,	10	,,	10	,,
20	,,	20	,,	20	,,	20	,,
30	,,	30	,,	30	,,	30	,,
40	,,	40	,,	40	,,	40	,,
50	6.79	50	,,	50	6.80	50	,,
60	,,	60	6.47	60	,,	60	6.41
70	,,	70	,,	70	,,	70	,,
80	,,	80	,,	80	,,	80	,,
90	,,	90	,,	90	,,	90	,,
100	,,	100	,,	100	,,	100	,,
130	,,	110	,,	110	,,	110	,,
160	,,	120	,,	120	,,	120	,,
190	,,	120	,,	130	,,	130	,,
220	6.78	140	,,	140	,,	140	,,
250	,,	150	,,	150	,,	150	,,
280	,,	160	6.46	160	,,	160	6.40
310	6.77	170	,,	170	,,	170	,,
340	,,	200	,,	180	6.79	200	,,
370	,,	230	,,	190	,,	230	6.39
400	6.76	290	6.45	200	,,	290	,,
430	,,	350	,,	230	,,	350	,,
460	,,	370	,,	260	,,	370	,,
490	6.74	390	,,	290	6.77	390	6.37
520	,,	410	6.43	310	,,	400	,,
550	,,	430	,,	340	,,	430	,,
580	6.73	450	,,	370	,,	450	6.36
610	,,	470	6.42	400	6.76	470	,,
After 4 hours.	6.50	After 4 hours	6.24	After 4 hours.	6.55	After 4 hours	6.22

pH. In what follows, therefore, the initial reading for the E.M.F. was taken as the true value.

As regards agreement in repeat measurements, Table II gives the results of a few determinations for two samples of fresh latex—A and B—and latices prepared from each of these by dilution with distilled water, as before in the proportion latex : water = 1 : 9. The *procedure was to stir the bulked latex thoroughly and then pour* about 15 c.cs into each of a series of glass tubes of approximately the same diameter in order that uniform conditions might obtain. Measurements were then carried out at definite intervals of time for each member of this series of samples. It will be seen that the values for latex, both diluted and undiluted, remain fairly constant within a period of about half-an-hour, which period is of course ample in practice for the performance of several determinations of pH.

TABLE II.

AGREEMENT IN READINGS FOR A SERIES OF SAMPLES TAKEN FROM THE SAME LATEX.

LATEX SAMPLE A.				LATEX SAMPLE B.			
UNDILUTED.		DILUTED 1.9.		UNDILUTED.		DILUTED 9.	
Time Mins.	pH.	Time Mins.	pH.	Time. Mins.	pH.	Time Mins.	pH.
0	6.80	0	6.52	0	7.01	0	6.77
5	6.81	12	6.52	5	7.00	10	6.77
10	6.79	27	6.51	10	7.01	21	6.75
15	6.80	37	6.52	15	7.00	30	6.76
20	6.80	47	6.54	20	7.01	35	6.77
25	6.80	66	6.52	25	7.02	45	6.77
30	6.81	77	6.54	30	7.00	65	6.76
35	6.79	85	6.53	35	7.01	80	6.75

In what follows, before each determination of pH, it was found necessary to rinse the negative electrode with distilled water and to heat the platinum to redness in a sulphur-free flame.

EXPERIMENTAL.

A. FRESH LATEX.

If latex is examined within about 2 hours after its exudation from the tree it is found to be very nearly neutral. The pH values of a large number of samples collected at various periods of the year ranged from 7.02 to 6.80. If the latex is allowed to stand so that its surface is exposed to the atmosphere, for the first 5 or 6 hours after tapping the pH remains very nearly constant. Thereafter clotting commences, accompanied by a more rapid increase in hydrogen ion concentration, until finally within a period of about 24 hours coagulation takes place. The coagulation is not, however, usually complete, that is to say, one does not find only a coherent coagulum floating in a clear serum. If the storage vessel is of sufficient depth one finds on the surface a shallow layer of thick alkaline slime of fairly high rubber content, then a deeper layer of coherent coagulum, and beneath a watery serum with a distinctly acid reaction, usually milky and still containing a few latex particles in suspension. In Table I the figures for undiluted latex show the course of the changes in hydrogen ion concentration within the first 4 hours after tapping. It is not possible to measure with a great degree of accuracy by the quinhydrone electrode the pH of the various layers which form as the result of this spontaneous coagulation since the changes are accompanied by a free evolution of hydrogen sulphide gas which may bring about poisoning of the electrodes. By means of indicators, however, it was ascertained that the pH of the surface layer was in the cases examined distinctly on the alkaline side of neutrality—from 7.5 to 8.0—while the pH of the serum resulting from the coagulation ranged from 6.3 to 6.5.

If a series of latex samples is prepared and examined in order of increasing hydrogen ion concentration it is found that there is first a range of pH values defining a condition of the sol which may be described as complete dispersion. By this is meant that no aggregation of the latex particles sufficient to cause separation of the whole or part of the disperse phase has taken place. This is followed by a range or zone within which the latex is coagulated. For still higher values of hydrogen ion concentration there is again a zone of complete dispersion and finally at the end of the scale a further range within which coagulation is again complete. As will be shown, later, the degree of dispersion in the various zones is influenced by several factors, principally by the rubber content of the latex, the transition from one zone or range to another is gradual, and, depending on the dilution of the latex, another set of values defining a condition intermediate between coagulation and dispersion may be obtained. Such a discontinuity has been observed in the flocculation of other colloidal sols by electrolytes—e.g. the flocculation of a negatively charged sol of mastic by $AlCl_3$—and these phenomena have been designated by the term " irregular series."

In studying the different zones defining various conditions of the dispersion, the procedure was to add increasing quantities of an acid coagulant in fixed concentration to a series of latex samples of equal volume and to examine the samples after a period of 24 hours. By choosing coagulation vessels of the same shape and dimensions for each member of the series, conditions under which changes in the pH of the system might occur within the period allowed for examination were kept as uniform as possible. Within such a period sufficient time is allowed for changes that occur in the dispersion to reach a stage at which they can be definitely characterised by their appearance and other properties. For example, the initial stages in coagulation may occur four hours after the addition of the coagulant without the visible separation of the latex into two layers, coagulum and serum. It is therefore difficult to characterise the condition of the dispersion at this stage. After a further period, however, the process may have reached a stage at which separation into coagulum and serum is distinctly discernible, and where from the appearance of the serum the coagulation may be described as partial or complete, as the case may be. By the addition of the coagulant in the manner stated the initial dry rubber content of the latex is lowered, but the concentration of the coagulant was so chosen that the dilution of the latex caused by its addition was very slight. When a greater interpolation of pH values was required for the transition from one boundary to another, a suitable buffer salt solution was added to the latex before the addition of the coagulant.

In tabulating the results the following system is adopted for the description of the condition of the dispersion after the period stated.

Complete Dispersion.—This describes a condition where the latex is homogeneous and completely liquid having the same appearance microscopically as pure latex examined soon after tapping. The particles are in vigorous Brownian motion and aggregation of the particles has not occurred to such an extent that there is a separation of rubber from the dispersion either in the form of a flocculate or a coherent clot of coagulum.

Partial Flocculation.—There is a separation from the dispersion of floccules which can be seen microscopically to consist of large aggregates of smaller rubber particles. The separation to the surface in the form of a flocculate is not complete, the underlying serum being milky in appearance and still containing a high proportion of rubber particles in suspension. The flocculate can be re-dispersed by shaking the tube and separation does not thereafter recommence for a considerable time.

Complete Flocculation.—The separation of rubber from the latex in the form of a flocculate is complete, the underlying serum being water-clear and practically free from rubber globules in suspension. As in the case of partial flocculation the same remarks apply to the reversibility of the flocculate.

Partial Coagulation.—There is a separation in the form of a coherent coagulum or clot, but a large proportion of rubber remains in suspension in the serum which is milky-white in appearance.

Coagulation almost complete.—There is a separation in the form of a coherent irreversible coagulum but the separation is not complete. The underlying serum is slightly cloudy and still contains a small proportion of rubber particles in suspension.

Complete Coagulation.—There is complete separation in the form of a coherent coagulum and a clear serum.

In Diagram I an attempt has been made to present the salient features differentiating the various conditions described above. The diagram has been constructed from the data set forth for the third series in Table III which will be discussed later.

LATEX OF 4 PER CENT. RUBBER CONTENT.

By working with latex of low rubber content it is possible to demonstrate more clearly than with undiluted latex the gradual changes which accompany the transition from one zone to another. Fresh latex was diluted to a dry rubber content of 4 per cent. and buffered with a 10 per cent. solution of ammonium acetate before the addition of the coagulant in the form of a 2.5 per cent. solution of acetic acid.

The buffer solution was added in three different proportions and corresponding to each proportion a separate series of latex samples was prepared. Table III summarises the results obtained. In the first series complete coagulation occurs at a pH of 4.81, in the second at pH of 4.84 and in the third at pH of 4.83. It will be seen that the transition from a condition of complete dispersion, or from the first liquid zone to the first coagulation zone is accompanied by a progressive series of changes. With increasing hydrogen ion concentration we pass through intermediate stages of partial coagulation, before complete coagulation results. The third series gives the clearest picture of what occurs since here the gradations in pH are smaller. By reference to Table III and to Diagram I it will be seen that the transitional stage is defined by the range pH 5.30 to 4.91.

On repeating this experiment with latex collected from the same group of trees on different days, different results were obtained, for the pH values defining the commencement of complete flocculation and of complete coagulation. Table IV shows how these values vary. The transition is irregular and somewhat ill-defined. Taking the average of the values obtained one finds that complete flocculation commences at pH 5.03 and complete coagulation at pH 4.87. Van Harpen, (2) working in Sumatra, finds for latex of approximately the same rubber content the values pH 5.05 and pH 4.77 respectively. It is probable that differences in latex composition are responsible.

In order to bring the latex into the second liquid zone or second zone of complete dispersion a stronger acid is required as coagulant.

TABLE III.

Fresh Latex.

Dry Rubber Content = 4 per cent.

First Liquid Zone to First Coagulation Zone.

c. c of 2.5 per cent. Acetic acid per 50 c.c latex.	c.c of 10 per cent. Ammonium acetate per 50 c.c latex.	Condition after 24 hours.	pH.
0.2	0.5	Partial flocculation	5.29
0.4	,,	,,	5.16
0.6	,,	,,	5.03
0.8	,,	,,	5.01
1.0	,,	Coagulation almost c'plete	4.98
1.2	,,	,,	4.89
1.4	,,	Complete coagulation	4.81
1.6	,,	,,	—
1.8	,,	,,	—
2.0	,,	,,	—
0.2	1.0	Partial flocculation	5.32
0.4	,,	,,	5.20
0.6	,,	,,	5.13
0.8	,,	Complete flocculation	5.08
1.0	,,	,,	4.96
1.2	,,	Coagulation almost c'plete	4.91
1.4	,,	Complete coagulation	4.84
1.6	,,	,,	—
1.8	,,	,,	—
2.0	,,	,,	—
2.2	,,	,,	—
2.4	,,	,,	—
2.6	,,	,,	—
2.8	,,	,,	—
3.0	,,	,,	—
3.2	,,	,,	—
3.8	,,	,,	—
4.0	,,	,,	—
0.2	1.5	Complete dispersion	6.02
0.6	,,	,,	5.70
0.8	,,	,,	5.55
0.9	,,	,,	5.45
1.0	,,	Partial flocculation	5.30
1.3	,,	,,	5.20
1.5	,,	,,	5.13
1.8	,,	,,	5.09
2.0	,,	Complete flocculation	5.01
2.2	,,	,,	4.93
2.5	,,	Coagulation almost c'plete	4.91
2.8	,,	Complete coagulation	4.83
3.0	,,	,,	4.81
3.5	,,	,,	4.73
3.7	,,	,,	4.69
4.0	,,	,,	4.66
4.5	,,	,,	4.63
4.7	,,	,,	4.56

This also applies for latex within the second zone of coagulation. Table V shows the results obtained using hydrochloric acid. It will be seen that the transition from one zone to another is not accompanied by so many changes in the state of dispersion as is the case when passing from the first liquid zone to the first coagulation zone, and the ranges of pH defining the transitional stages are smaller. The flocculated condition does not make its appearance although the gradations in pH are small. Taking the series in order of increasing hydrogen ion concentration, in the passage from the first coagulation zone to the second liquid zone a condition of complete dispersion first makes its appearance at pH 3.52, and this condition persists *until a pH of 0.83 is reached, until complete coagulation results at a* pH value of 0.82.

The foregoing results are conveniently summarised in Table VI.

TABLE IV.

FRESH LATEX.

Dry Rubber Content 4 per cent.

Date of tapping	pH. Complete Flocculation.	pH. Complete Coagulation
22-6-29	5.01	4.74
23-6-29	5.08	4.78
24-6-29	4.98	4.93
25-6-29	5.11	4.96
1-7-29	5.00	4.87
3-7-29	4.95	4.84
4-7-29	5.03	4.74
5-7-29	5.02	4.88
15-7-29	4.96	4.88
18-7-29	5.02	4.87
19-7-29	5.14	5.04
Average	5.03	4.87

TABLE V.

Fresh Latex.

Dry Rubber Content=4 per cent.

First Coagulation Zone to Second Liquid Zone.

c. c of $\frac{N}{10}$ H. Cl per 50 c. c. latex.	Condition after 24 hours.	pH.
0.5	Incomplete flocculation	—
1.0	,,	—
1.5	Complete coagulation	4.74
2.0	,,	—
2.5	,,	3.80
2.6	Coagulation almost complete	3.71
2.7	,,	3.65
2.9	,,	3.58
3.0	Complete dispersion	3.52
3.5	,,	3.20

Second Liquid Zone to Second Coagulation Zone.

c. c of N. H Cl. per 50 c. c. latex.	Condition after 24 hours.	pH.
0.8	Complete Dispersion	2.01
4.8	,,	1.26
6.0	,,	1.00
7.0	Partial Coagulation	0.88
8.0	,,	0.87
9.0	,,	0.83
10.0	Complete Coagulation	0.82
11.0	,,	0.76
12.0	,,	0.74
13.0	,,	0.71
14.0	,,	0.67
15.0	,,	0.66
16.0	,,	0.62

TABLE VI.

Fresh Latex.

Dry Rubber Content=4 per cent.

—	pH Range.
Complete Dispersion, ...	>5·30
Partial Flocculation, ...	5·30 — 5·01
Complete Flocculation, ...	5·01 — 4·91
Coagulation almost complete, ...	4·91 — 4·83
Complete Coagulation, ...	4·83 — 3·80
Coagulation almost complete, ...	3·80 — 3·52
Complete Dispersion, ...	3·52 — 1.00
Partial Coagulation, ...	1.00 — 0.82
Complete Coagulation, ...	<0.82

Latex of 15 per cent. Rubber Content.

Dilution of the latex to a rubber content of 15 per cent., which is the standard dilution usually adopted in Malayan plantation practice, does not create very marked differences as compared with latex of greater dilution in the ranges of pH values defining the various zones in the irregular series. As will be seen from Tables VII and VIII and Table IX which summarises the results, there is a more extended range of values within which complete coagulation takes place in the first zone, and the range for flocculation is smaller. The first appearance of a flocculate occurs at pH 5.54 whereas in the previous case the lower value of 5.30 is required to bring about the first evidence of coagulation.

TABLE VII.

FRESH LATEX.

Dry Rubber Content = 15 per cent.

First Liquid Zone to First Coagulation Zone.

c. c of 2.5 per cent. acetic acid per 50 c.c of latex.	c. c of 10 per cent. ammonium acetate per 50 c.c of latex.	Condition after 24 hours.	pH.
0	1.0	Complete Dispersion	6.96
0.2	,,	,,	6.20
0.6	,,	,,	5.82
1.0	,,	Partial Flocculation	5.54
1.2	,,	,,	—
1.4	,,	,,	—
1.8	,,	Coagulation almost complete	5.24
2.0	,,	,,	—
2.2	,,	,,	—
2.4	,,	,,	5.04
2.6	,,	,,	4.94
3.0	,,	,,	4.82
3.5	,,	Complete Coagulation	4.78
3.8	,,	,,	—
4.0	,,	,,	—

First Coagulation Zone to Second Liquid Zone.

c. c of $\frac{N}{1}$ H.Cl. per 50 c.c of latex.	Condition after 24 hours.	pH.
0.2	Complete Dispersion	—
0.4	Coagulation almost complete	—
0.6	Complete Coagulation	—
0.8	,,	—
1.0	,,	3.70
1.2	,,	3.51
1.3	Coagulation almost complete	3.24
1.4	,,	3.01
1.5	Complete Dispersion	3.00
2.0	,,	—
3.0	,,	—

TABLE VIII.

Fresh Latex.

Dry Rubber Content = 15 per cent.

c. c of 10 N. HCl per 50 c. c of latex.	Condition after 24 hours.	pH.
0.2	Complete Dispersion	1.62
0.4	,,	—
0.6	Partial Coagulation	1.23
0.8	,,	—
1.0	,,	0.95
1.5	Complete Coagulation	0.74

TABLE IX.

Fresh Latex.

Dry Rubber Content = 15 per cent.

——	pH Range.
Complete Dispersion	>5·54
Partial Flocculation	5·54 — 5·24
Coagulation almost complete ...	5·24 — 4·78
Complete coagulation	4·78 — 3·51
Coagulation almost complete ...	3·51 — 3·01
Complete Dispersion	3·01 — 1·23
Partial Coagulation	1·23 — 0·73
Complete Coagulation	<0·73

LATEX OF 20 PER CENT. RUBBER CONTENT.

For the sake of brevity the detailed experimental results are not reproduced for latex diluted to a rubber content of 20 per cent. and Table X gives a summary. From this it will be seen that there is now a marked difference in the progress of the series. In the first place coagulation makes its appearance at a higher value than in the two preceding cases viz. at pH 5.80. But the main difference is found in the range of values within which latices of greater dilution are in the condition defined by the second liquid zone. With latex of 20 per cent. dry rubber content, between pH 3.02 and 0.60, a small clot of coherent coagulum is formed, although the rest of the latex remains in a state of complete dispersion. The percentage of the total rubber content separating as a clot was found to be roughly 2 per cent. the rest remaining in stable dispersion in the serum. There is, therefore, strictly speaking, no second liquid zone with latex of this rubber content. It will be seen also that a slightly higher hydrogen ion concentration is required before complete coagulation appears in the second coagulation zone—viz. pH 0.60—and that a region of flocculation does appear.

TABLE X.

FRESH LATEX.

Dry Rubber Content=20 per cent.

—	pH Range.
Complete Dispersion	>5.80
Coagulation almost complete ...	5.80 — 4.84
Complete Coagulation	4.84 — 3.51
Coagulation almost complete ...	3.51 — 3.02
Partial Coagulation	3.02 — 0.60
Complete Coagulation	<0.60

LATEX OF RUBBER CONTENT=35 PER CENT.

Undiluted field latex was used for the tests and the differences here are very marked. The detailed results of a typical experiment are set out in Table XI and summarised in Table XII. Here coagulation first appears at a still higher value than in previous cases—

viz. pH 6.24—and flocculation does not occur. There is no second liquid zone. Within the range defined by pH 3.02 to 0.83, coagulation is almost complete and the serum is slightly milky. There are, therefore, only two zones in the series—a liquid zone and a coagulation zone.

TABLE XI.

FRESH LATEX.

Dry Rubber Content = 35 per cent.

c. c of 2.5 per cent. acetic acid per 50 c.c of latex.	c.c of 10 per cent. ammonium acetate per 50 c.c. of latex.	Condition after 24 hours.	p.H.
0.5	0.5	Complete Dispersion	6.31
1.0	,,	Partial Coagulation	6.20
2.0	,,	,,	—
3.0	,,	,,	—
4.0	,,	,,	—
5.0	,,	Complete Coagulation	4.71
7.0	,,	,,	—
c.c of N.HCl per 50 c.c. of latex.			
0.05	Nil	Complete Dispersion	6.28
0.2	,,	Partial Coagulation	6.24
0.3	,,	,,	—
0.4	,,	,,	—
0.5	,,	,,	5.31
1.0	,,	Complete Coagulation	4.49
2.0	,,	,,	3.37
2.2	,,	Coagulation almost c'plete	3.02
2.4	,,	,,	2.78
2.5	,,	,,	2.65
3.2	,,	,,	2.11
3.4	,,	,,	—
3.6	,,	,,	1.91
3.8	,,	,,	—
4.0	,,	,,	1.53
4.5	,,	,,	—
5.0	,,	,,	1.28
5.5	,,	,,	—
6.0	,,	,,	1.16
c.c of 10 N.HCl per 50 c.c of latex.			
1.0	Nil	Coagulation almost c'plete	—
1.5	,,	Complete Coagulation	0.83
2.0	,,	,,	—

TABLE XII.

FRESH LATEX.

Dry Rubber Content = 35 per cent.

——	pH Range.
Complete Dispersion	>6.24
Partial Coagulation	6.24 — 4.71
Complete Coagulation	4.71 — 3.02
Coagulation almost complete ...	3.02 — 0.83
Complete Coagulation	<0.83

B. HEATED LATEX.

A study of the progress of changes for latex which has been boiled or pasteurised shows certain deviations from the normal course of the irregular series for pure field latex. Preparation was carried out according to the method which de Vries and Beumée-Nieuwland (5) adopt for boiled latex or "B" liquid. This was carried out by boiling nine volumes of water and quickly pouring in one volume of latex, boiling the mixture for a further period of three minutes and then allowing to stand for five minutes before cooling in running water to the temperature of the room. Latex so prepared remains as a fairly stable dispersion for several days. Experimental work with this latex was carried out on the day of preparation and the definitions adopted for the various states of dispersion are the same as those described for fresh latex.

To a portion of this "B" liquid, a solution of sodium oleate was added so that the concentration of soap in the latex was 0.01 per cent. by volume.

A sample of pure field latex diluted to the same rubber content, viz. 4 per cent, was treated similarly.

A comparison was then made between the three samples (1) "B" liquid, (2) "B" liquid + 0.01 per cent. of sodium oleate (3) Fresh latex + 0.01 per cent. of sodium oleate. The experimental results are summarised in Table XIII.

The observations of other workers, notably de Vries (6) and Belgrave, (7) are confirmed to the effect that "B" liquid merely flocculates for values of pH, for which fresh latex coagulates within the first coagulation zone. Coagulation does not occur until a pH of 0.80 is reached, a value which is practically the same as that observed for pure field latex. For "B" liquid the definitive values of pH for the various zones agree closely with those obtained by van Harpen (2).

By the addition of a small quantity of sodium oleate to "B" liquid, however, coagulation takes the same course as for pure latex—between pH 4.68 and 3.50 complete coagulation is obtained. In other words the addition of sodium oleate has brought about a coalescence of the floccules.

As compared with pure field latex of the same dilution it will be seen from Table XIII Column (3) that the addition of sodium oleate has caused the first appearance of separation from the dispersion to commence at a slightly lower hydrogen ion concentration viz. pH 5.24. Also coagulation is first complete at pH 4.95 as compared with the value 4.83 for pure latex.

During the course of this work it was noted that there is on occasions a slight rise in pH on heating. Samples were prepared from the same stock of fresh latex in the same way as for "B" liquid except that the temperature of heating was varied from room temperature (29°C) to 100°C. The measurements of pH were carried out when all the samples of the series had cooled to room temperature. Other conditions during preparation were kept as uniform as possible for each member of the series. Table XIV which gives the results obtained for two series prepared from different stock latices, A and B, shows that the pH tends to increase as the temperature of heating increases. The two cases quoted are, however, extreme. With some samples the rise in pH was very slight, although in all cases it was appreciable. A possible explanation is that carbon dioxide is lost from the system on heating thereby decreasing the acidity. Another factor which possibly acts in conjunction with the loss of carbon dioxide is the rise of pH which may take place as a result of denaturation of the proteins, since almost certainly some of the proteins are denatured by heating the latex to a high temperature. A rise of pH taking place as the result of the heat denaturation of egg albumin solutions has been observed by Chick and Martin (8).

TABLE XIII.

Condition	Ranges of pH. (1) "B" Liquid	(2) "B" Liquid +0.01 per cent. of Sodium oleate.	(3) Fresh Latex +0.01 per cent. of Sodium oleate.
Dispersion -	> 5.02	> 5.01	> 5.24
Flocculation -	5.02 - 3.52	5.01 - 4.68	5.24 - 4.95
Coagulation -	Does not occur	4.68 - 3.50	4.95 - 3.51
Dispersion -	3.52 - 0.80	3.50 - 0.82	3.51 - 0.83
Coagulation -	< 0.80	< 0.82	< 0.83

TABLE XIV.

Latex A		Latex B	
Temperature of Heating °C.	pH at 28°C.	Temperature of Heating °C.	pH at 28°C.
28	6.68	28	5.92
35	6.70	35	5.93
40	6.73	40	5.94
45	6.77	43	5.99
51	6.82	50	6.41
55	6.91	55	6.52
60	6.91	62	6.61
65	6.86	65	6.61
70	6.90	70	6.62
76	6.91	75	6.62
80	6.99	80	6.62
90	6.99	90	6.62
100	7.19	100	6.64

C. Preserved Latex.

The normal course of the irregular series observed for fresh field latex is markedly altered by the addition of certain preservative substances. The preservative most widely used in plantation practice is ammonia, but other substances are occasionally employed chief among which are sodium hydroxide and formalin. The various preserved latices were diluted to a rubber content of 4 per cent. since at this dilution comparison of the effect of each preservative substance on coagulation is easily made, and, as with fresh field latex, the transitional stages between the various zones are easily defined. The acid coagulants used were the same for all samples examined.

(a) *Ammonia.*—The samples were prepared by the addition of a solution of ammonia of 0.891 specific gravity to fresh field latex, the concentrations of NH_3 in the various samples ranging from 0.30

to 0.80 per cent. by weight, at the time of preparation. The samples were examined a few days after preparation and at intervals of about one month during a period of storage of ten months. It was found that differences in the period of storage and the quantity of ammonia added did not affect the ranges of hydrogen ion concentration defining the various states of dispersion in the coagulation series. For the sake of brevity the detailed experimental results are not reproduced and the results are summarised in Table XV. Column (1) gives results which are typical of those obtained with all the samples of ammoniated latex. It will be seen that the results are almost the same as those obtained for pure field latex of the same dilution. This applies also to ammoniated latex of higher rubber content although with undiluted latex there is a difference in behaviour after the addition of the coagulant. With undiluted ammoniated latex coagulation is obtained almost immediately after the addition of the acid. The first few drops of acid produces local clotting even when the latex is thoroughly stirred during its addition, and with increasing quantities this clot increases in size until coagulation is complete. With pure latex, however, no such local clotting is observed and several hours must elapse before coagulation is obtained. It may be stated therefore that ammoniated latex is more sensitive than pure latex to acid coagulants.

(b) *Sodium Hydroxide.*—The sample examined was prepared by adding a concentrated solution of sodium hydroxide to field latex to give a latex containing 0.8 per cent. by weight of sodium hydroxide. The interesting feature is that the course of coagulation is affected by the length of the period of storage. When examined within two or three days after the addition of the preservative it was found that coagulation did not take place for any value of pH below 7.0 within a period of 24 hours after the addition of the coagulant. In other words within this specified period the latex does not coagulate whatever its hydrogen ion concentration. As will be seen from Table XV column (2) which gives the results obtained on examination of the sample 2 days after the addition of the preservative, the latex merely flocculates for values of pH at which fresh field latex coagulates, both in the first and in the second coagulation zones. There are two zones of flocculation in place of two zones of coagulation, separated by zones of complete dispersion. Latex within these flocculation zones remains in that state for several days without any evidence of coherent clot formation, but later the floccules gradually cohere and coagulation ensues. This applies also to sodium hydroxide latex of high rubber content. After the addition of the coagulant a coherent coagulum can be obtained only by mechanical kneading of the flocculated mass.

When the same sample of latex treated with sodium hydroxide was examined after a longer period of storage it was found that two zones

TABLE XV.

PRESERVED LATEX.

Dry Rubber Content = 4 per cent.

Ammonia.	*Sodium hydroxide.* Fresh.	*Sodium hydroxide* Long Storage.	*Formalin.*
Complete Dispersion > 5.30 Partial Flocculation 5.30 - 5.01 Complete Flocculation 5.01 - 4.92 Coagulation almost complete 4.92 - 4.81 Complete Coagulation 4.81 - 3.79 Coagulation almost complete 3.79 - 3.51 Complete Dispersion 3.51 - 1.02 Partial Coagulation 1.02 - 0.82 Complete Coagulation < 0.82	Complete Dispersion > 5.69 Partial Flocculation 5.69 - 4.78 Complete Flocculation 4.78 - 3.39 Partial Flocculation 3.39 - 3.00 Complete Dispersion 3.00 - 1.01 Partial Flocculation 1.01 - 0.63 Complete Flocculation < 0.63	Complete Dispersion > 8.00 (Approx.) Partial Coagulation 8.00 - 4.76 Complete Coagulation 4.76 - 3.01 Partial Coagulation 3.01 - 1.03 Coagulation almost complete 1.03 - 0.63 Complete Coagulation < 0.63	Complete Dispersion > 4.56 Partial Flocculation 4.56 - 4.36 Complete Flocculation 4.36 - 3.41 Partial Flocculation 3.41 - 3.27 Complete Dispersion 3.27 - 1.07 Partial Flocculation 1.07 - 0.66 Complete Flocculation < 0.66

of complete coagulation were obtained as for fresh field latex. Column (3) gives the results for a period of six months' storage. These are typical of those obtained when the latex was examined at intervals of one month after preparation. It is only when freshly prepared that such latex shows abnormal coagulation. Although normal coagulation is restored after longer storage, the latex is very sensitive to acid coagulants, for local clotting takes place immediately after the addition of the acid even when the latex is dilute and at low values of pH. It is thus still more sensitive than ammoniated latex. As will be seen from the table, clotting or partial coagulation commences at a pH well on the alkaline side of neutrality, viz. 8.00, although this value is approximate and had to be obtained colorimetrically by means of indicators, the quinhydrone electrode being inapplicable to solutions with a pH greater than 8.0.

It will also be seen that there is no second liquid zone. Between the range pH 3.01 and 1.03, which defines a state of complete dispersion in the case of pure latex, sodium hydroxide latex partially coagulates, approximately 50 per cent. of the total rubber separating from the dispersion in the form of a coherent clot.

(c) *Formalin.*—Latex preserved by the addition of formalin behaves in much the same way as fresh latex treated with sodium hydroxide. The sample under discussion was prepared by the addition of a solution of formalin to give a concentration of formaldehyde in the latex of 0.4 per cent. by volume and the results given in column (4) of Table XV refer to the examination of the sample after a period of four months' storage. As with freshly prepared latex sodium hydroxide coagulation does not occur within a period of 24 hours when the latex is diluted to a rubber content of 4 per cent. whatever the period of storage. Comparing the ranges of pH in column (4) with those in column (2) it will be seen that there are in both cases two zones of flocculation separated by two zones of complete dispersion, although in the case of latex treated with formalin the first appearance of the flocculation stage is associated with a higher hydrogen ion concentration—pH 4.56 for formalin and 5.69 for sodium hydroxide. Otherwise the behaviour of these two preserved latices is very similar.

(d) *Centrifuged Latex.*—When latex is subjected to centrifugal action, for example in a centrifuge of the de Laval type, separation into two latex fractions takes place. Owing to the difference in the specific gravities of the rubber particles and the dispersion medium, when the bowl of the centrifuge is rotated at a sufficiently high speed the rubber particles being lighter pass to the central axis of the bowl while the serum flows towards the outside walls. The separation is, however, not complete. The cream fraction has

TABLE XVI.

CENTRIFUGED LATEX.

Dry Rubber Content=4 per cent.

Cream Latex.	Skim Latex.
Complete Dispersion >5.30	Complete Dispersion >6.50
Partial Coagulation 5.30 — 4.62	Partial Flocculation 6.50 — 5.83
Complete Coagulation 4.62 — 3.31	Coagulation almost complete 5.83 — 5.28
Coagulation almost complete 3.31 — 2.51	Complete Coagulation 5.28 — 3.53
Partial Coagulation 2.51 — 0.73	Complete Dispersion 3.53 — 1.00
Complete Coagulation <0.73	Complete Flocculation 1.00 — 0.70
	Complete Coagulation <0.70

a high rubber content and contains a small proportion of serum substances, while the skim fraction is of relatively low rubber content and contains most of the serum constituents. The samples used in the experiment were obtained by separation in a Sharples super-centrifuge of field latex to which was added 1 per cent. by volume of a solution of ammonia of 0.891 specific gravity. The cream fraction had a dry rubber content of 55.2 per cent. and the skim fraction 10.3 per cent. It may be mentioned that this type of centrifuge was not found to be suitable for continuous work, although in the case under discussion separation was quite successful.

With the object of comparing the course of coagulation for these two fractions each was diluted to a rubber content of 4 per cent. and examined shortly after preparation. Table XVI which summarises the results obtained shows that there is a considerable difference in behaviour. With cream latex there is no second liquid zone or zone of complete dispersion. Between pH 2.51 and 0.73 slight clotting takes place and about one half of the total rubber present separates as a coherent clot. In behaviour it is very similar to undiluted field latex having a rubber content of 35 per cent. With the skim fraction, however, there are two zones of complete coagulation separated by two zones of complete dispersion, and the first evidences of separation commence at pH 6.50 at which flocculation sets in, whereas with cream latex coagulation commences at a lower value—viz. pH 5.30. Skim latex is peculiar in that there is a flocculation stage in the passage from the second liquid to the second coagulation zone—the range pH 1.00—0.70 defines a condition of complete flocculation. It will be noted that in all the preceding data cited for pure latex, the flocculation stage is associated only with the transition from complete dispersion to the first coagulation zone, and does not appear in the transitional stages between the other zones.

To summarise the experimental work described above an attempt has been made to illustrate graphically in Diagrams I, II, III and IV following a system which accords sufficiently well with the observed facts to bring out differences in the behaviour of the various latices. For this purpose the results have been arranged under three headings (a) Fresh Latex (b) Preserved Latex and (c) Centrifuged Latex. To illustrate the course of the irregular coagulation series for a particular latex the scheme adopted is to divide the abscissa into a scale of pH values and to divide the ordinate into an arbitrarily chosen scale representing the degree of dispersion in the various stages. The number 100 is chosen to represent a state of complete dispersion while zero represents a conditionn of complete coagulation. The scheme does not permit of numerical representation of conditions of the dispersion intermediate between these two extremes, but it does allow of comparison of the ranges of pH values defining the various zones and roughly of the comparative degree of dispersion within these zones.

The effect of dry rubber content on the continuity of the course of coagulation for fresh latex is also summarised in Table XVII compiled from the experimental results recorded under Section A.

TABLE XVII.

Fresh Latex.

State of Dispersion	Range of pH.			
	D.R.C. = 4 per cent.	D.R.C. = 15 per cent.	D.R.C. = 20 per cent.	D.R.C. = 35 per cent.
Complete Dispersion. -	> 5.30	> 5.54	> 5.80	> 6.24
Partial Flocculation -	5.30 - 5.01	5.54 - 5.24	—	—
Complete Flocculation -	5.01 - 4.91	—	—	—
Partial Coagulation -	—	—	—	6.24 - 4.71
Coagulation almost complete -	4.91 - 4.83	5.24 - 4.78	5.80 - 4.84	—
Complete Coagulation -	4.83 - 3.80	4.78 - 3.51	4.84 - 3.51	4.71 - 3.02
Coagulation almost complete -	3.80 - 3.52	3.51 - 3.01	3.51 - 3.02	3.02 - 0.83
Complete Dispersion -	3.52 - 1.00	3.01 - 1.23	—	—
Partial Coagulation -	1.00 - 0.82	1.23 - 0.73	3.02 - 0.60	—
Complete Coagulation -	< 0.82	< 0.73	< 0.60	< 0.83

CONCLUSIONS.

1. The continuity of the course of coagulation of (a) fresh field latex (b) preserved latex and (c) centrifuged latex by the addition of acids has been studied, and the pH values defining the various zones in the irregular series determined by means of the quinhydrone electrode.

2. In the case of fresh latex diluted to a rubber content of less than 10 per cent. the transition from the first liquid zone to the first coagulation zone is accompanied by a progressive series of changes in the state of the dispersion and is also rather irregular, variations in the pH values defining the transitional stages being found for latex harvested on different days. In most cases on examining the series in the direction of decreasing pH, there is a gradual progression from a state of complete dispersion to complete coagulation, through regions of partial flocculation, complete flocculation and incomplete coagulation, in that order. Generally

the range covered by this *transitional stage* is *from* pH 5.30, at which point a separation of the rubber component from the dispersion is first visible at pH 4.87 which marks the beginning of complete coagulation. These values agree fairly closely with those obtained by van Harpen (2).

3. The dry rubber content of fresh field latex exerts a marked influence on the course of the irregular series. With latices varying in rubber content from 4 to 35 per cent., the range of pH values defining the transitional stage between the first liquid and the first coagulation zones increases as the dry rubber content increases. On the other hand, with increasing rubber content the range of values defining a condition of flocculation decreases until with latices of a rubber content higher than approximately 15 per cent. this stage disappears altogether. It was also found that with latices of between 20 and 35 per cent. concentration there is no second zone of complete dispersion. Whereas the dispersion of latices of greater dilution is complete in the range covered by the second liquid zone —approximately pH 3.5 to 1.0—and will remain stable for several days provided the hydrogen ion concentration is kept constant, with latices of greater concentration than 20 per cent. coagulation takes place for approximately the same range of values, the extent of the coagulation depending on the rubber content.

4. Independent of the degree of dilution of fresh field latex the appearance of a flocculation stage is associated only with the transition from the first liquid zone to the first coagulation zone.

5. *The irregular series for boiled latex or "B" liquid* was studied and confirmation was obtained of observations made by other workers to the effect that such latex does not coagulate until a pH value of 0.80 is reached, and, moreover, that the addition of soaps such as sodium oleate restores normal coagulation in the first zone. This was compared with the effect of the addition of sodium oleate to fresh field latex diluted to the same rubber content as the "B" liquid. Measurement was made of the alteration in pH which occurs in fresh latex heated to various temperatures and allowed to cool to the initial temperature.

6. As regards the course of the irregular series it was found that latex preserved with ammonia behaves in much the same way as fresh field latex. In latex preserved with formalin, however, it was found that if the latex is diluted to a rubber content of less than 10 per cent. coagulation by acid does not occur for any value of pH below 7.0. For approximately the same ranges of values within which fresh latex of the same dilution shows two well marked coagulation zones, there correspond two zones of complete flocculation in the case of formalin preserved latex. Even when the latex is undiluted coagulation by acid takes place only after mechanical kneading of the flocculated mass. The same behaviour was noted for freshly

prepared latex treated with sodium hydroxide. On the other hand, when latex preserved with sodium hydroxide is stored for a month or more, normal coagulation is restored within these two zones although the course of the series is almost continuous, there being no second liquid zone. In such latex also, clot formation by the addition of acids can commence at a pH on the alkaline side of neutrality.

7. A study was also made of latex separated into 'cream' and skim' by centrifugal action. It was found that cream latex behaves in a similar manner to latex preserved with sodium hydroxide which has been stored for a month or more, in so far as there is practically no break in the continuity of the series. With the skim fraction on the other hand the irregularity of the series is just as well marked as in the case of fresh field latex. These remarks apply to latices diluted to a rubber content of 4 per cent.

ACKNOWLEDGMENT.

The writer desires here to record his appreciation of the valuable advice of his colleague Dr. C. F. Flint on the assembly of the apparatus used in these investigations.

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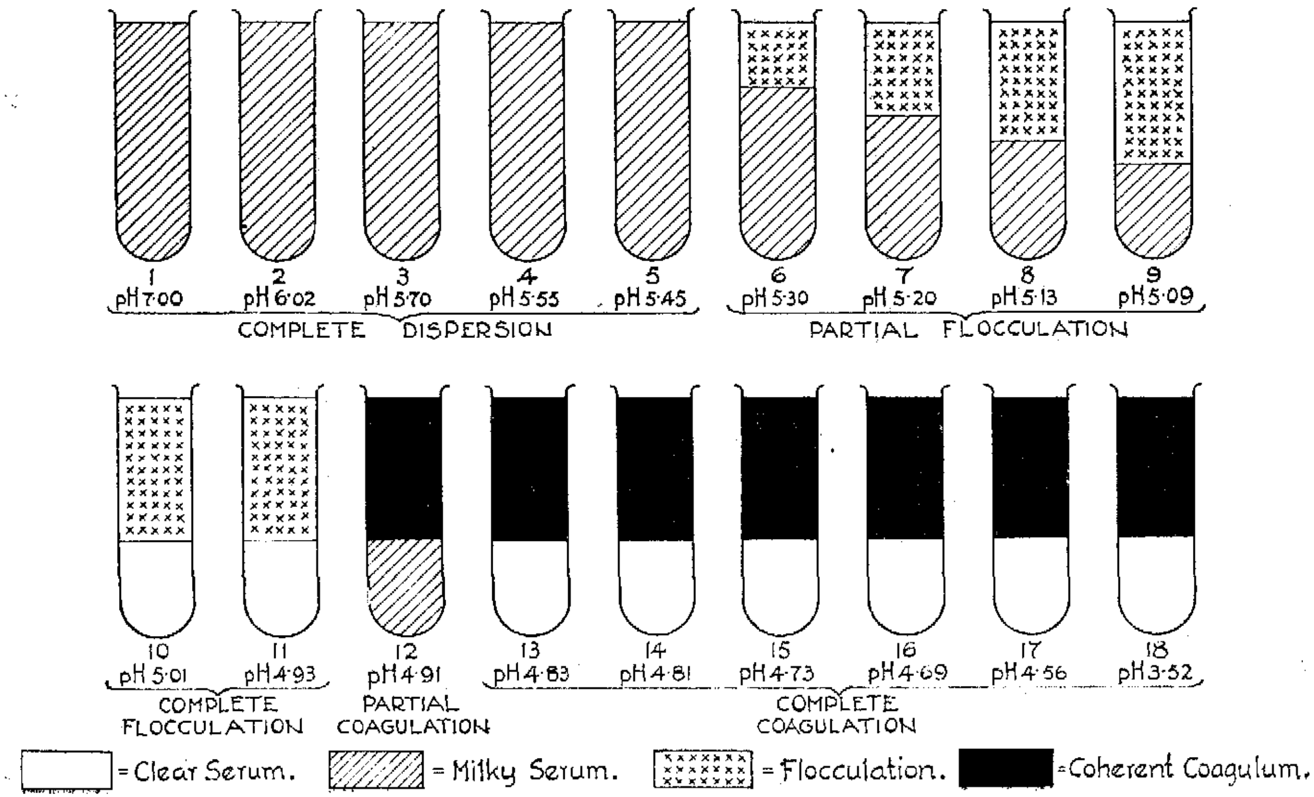
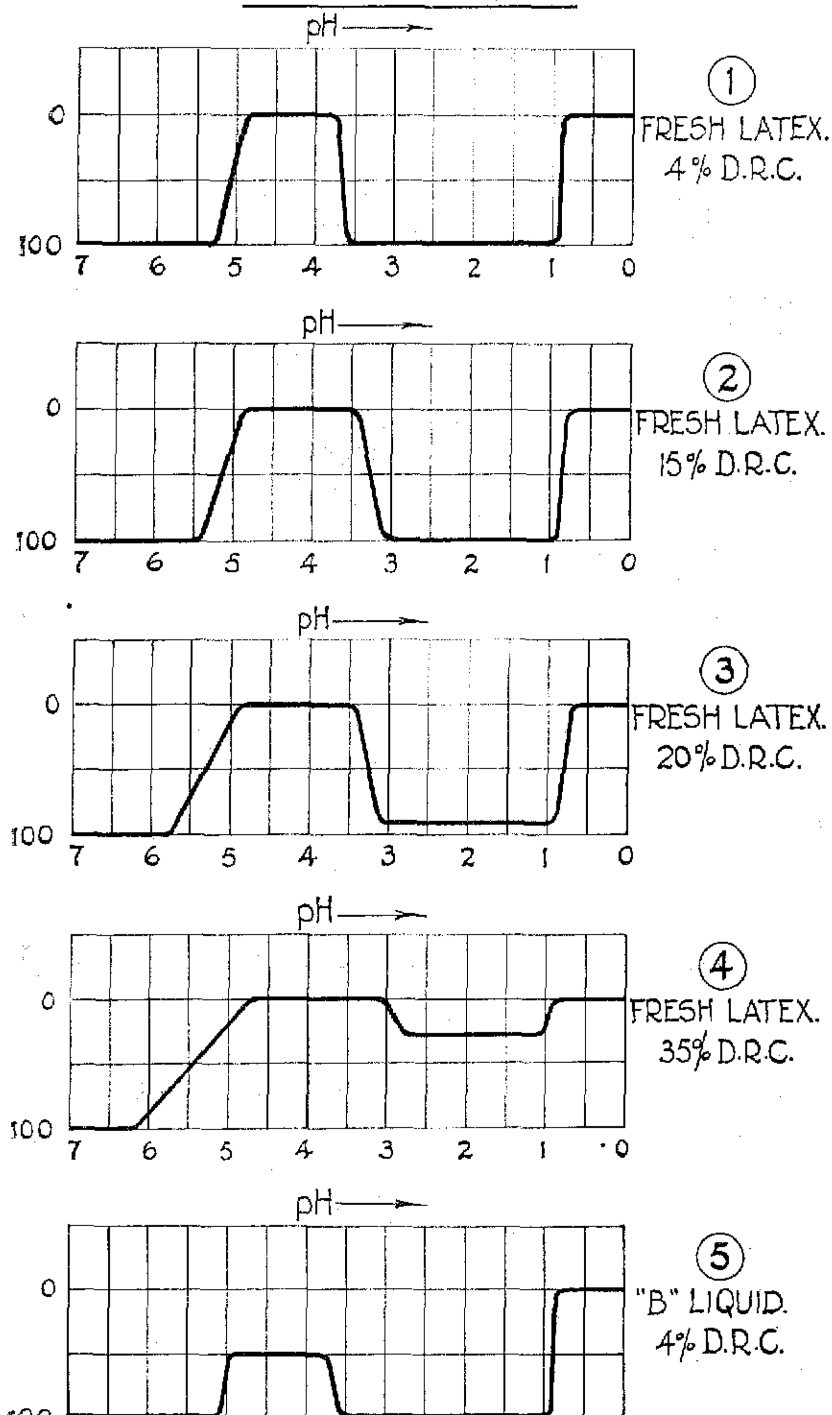


1 pH 7·00
2 pH 6·02
3 pH 5·70
4 pH 5·55
5 pH 5·45
6 pH 5·30
7 pH 5·20
8 pH 5·13
9 pH 5·09
COMPLETE DISPERSION
PARTIAL FLOCCULATION
10 pH 5·01
11 pH 4·93
12 pH 4·91
13 pH 4·83
14 pH 4·81
15 pH 4·73
16 pH 4·69
17 pH 4·56
18 pH 3·52
COMPLETE FLOCCULATION
PARTIAL COAGULATION
COMPLETE COAGULATION
= Clear Serum.
= Milky Serum.
= Flocculation.
= Coherent Coagulum.

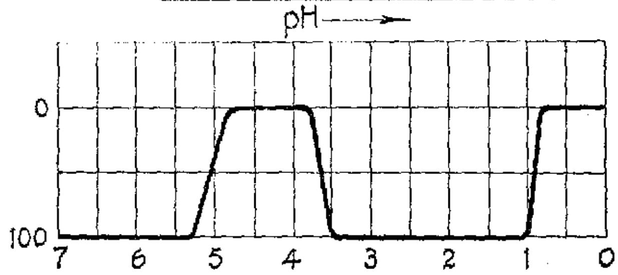
DIAGRAM – I.

FRESH LATEX.

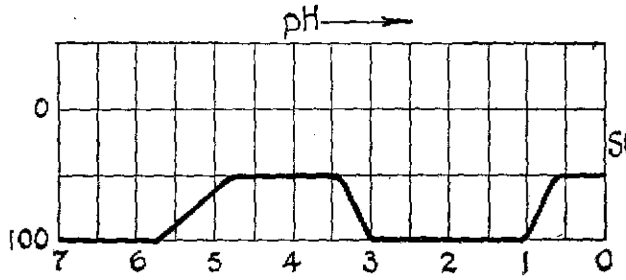


DIAGRAM—II.

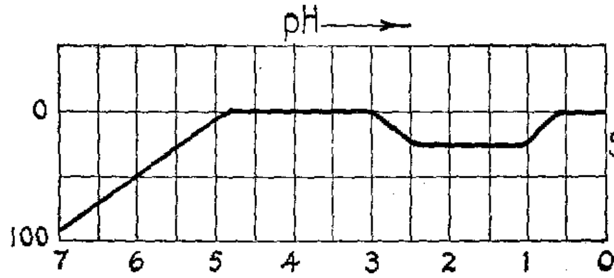
PRESERVED LATEX



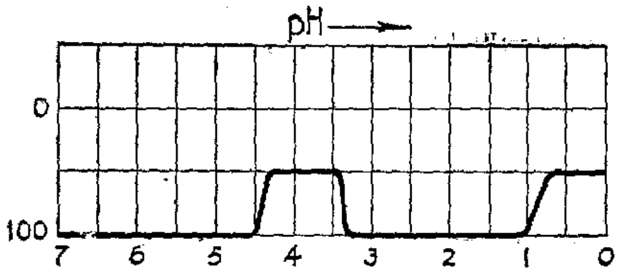
⑥
AMMONIA.
4% D.R.C.



⑦
FRESH
SODIUM HYDROXIDE
4% D.R.C.



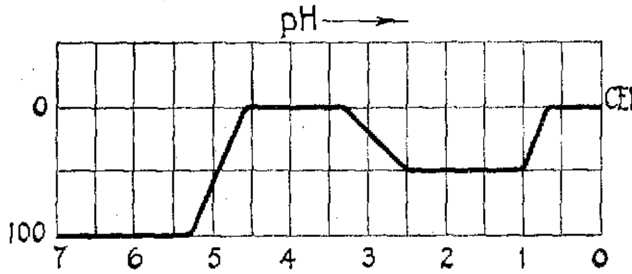
⑧
LONG STORAGE
SODIUM HYDROXIDE
4% D.R.C.



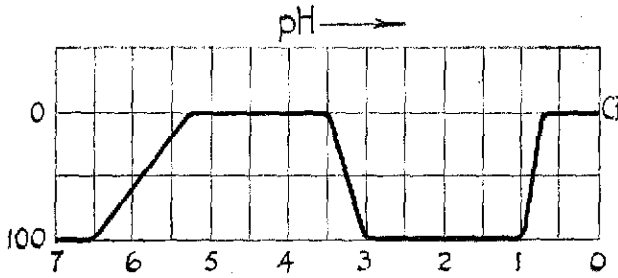
⑨
FORMALIN
4% D.R.C.

DIAGRAM—III.

CENTRIFUGED LATEX.



(10)
CENTRIFUGED LATEX
CREAM.
4% D.R.C.



(11)
CENTRIFUGED LATEX
SKIM.
4% D.R.C.

DIAGRAM — IV.