

COAGULATION STUDIES OF THE LATEX OF *CRYPTOSTEGIA* *GRANDIFLORA*, R. BR.—A WAR TIME SOURCE OF VEGETABLE RUBBER. PART I

15

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Studies on the coagulation of the latex of *Cryptostegia grandiflora* have been made with special reference to the hydrogen-ion concentration and the present paper embodies the results of auto-coagulation, auto-creaming, coagulation by heat, centrifuging, electric current, and water and those obtained by the action of chemical reagents on latex, e.g. mineral and organic acids, alkalis, bases, salts, reagents for coagulating proteins, hydration, dehydration and miscellaneous reagents like formaldehyde, lemon juice, curd and molasses. The observations show that rubber could be separated from the latex by the methods which are chemical as well as physical in nature.

The work was undertaken at the request from the Department of Supply with a view to evolving a method which would not require heavy expenditure of chemicals and will be workable by the same equipment used as in the case of *Hevea*.

With these objects in view the information has been collected with special reference to the hydrogen-ion concentration of the latex. The details of the methods are given in the experimental procedure.

Coagulation by Chemical Reagents.—Under this head are described the results of mineral and organic acids, alkalis, organic bases and salts and also special chemical reagents used for coagulating proteins and those which bring about hydration and dehydration. It is found that acids can coagulate the latex in a range which would require very small quantity of the coagulant and with an increase in acidity the percentage of coagulum would decrease. In most cases it is found that if the acidity reaches the limit which would drop the p_H of the latex from 4.6 to 4.0, the latex will not coagulate. Thus with a decrease of 0.6 in the value of p_H the latex is stabilised. Mineral and organic acids appear to be equally good and the coagulum produced has a good tensile strength and elasticity and can be sheeted. Organic acids from formic to butyric acid with an increase in the number of carbon atoms had no special advantage. The minimum quantities of acids, effective to coagulate a litre of latex, are given in Tables I and VIII ("The Science of Rubber" Eng. Ed., 1934, by Prof. K. Memmler, Translated by Dunbrook and Morris, New York, p. 121, 1934; P. Schidrowitz, "Rubber Recueil", 370**).

TABLE I
Coagulating effect of various substances

Coagulant.	Quantities per litre of 30% latex of <i>Hevea</i> with name of authors.				Quantities per litre of 2-7% of <i>Cryptostegia</i> latex by Siddiqui.
	Eaton.	Morgan.	Parkin.	Beadle & Stevens.	
Acetic acid	1.0 g.	1.0 g.	9.5 g.	1.5-6.0 g.	0.25-4 c.c.
Formic acid	0.6	0.8	4.5	...	0.25-2
Hydrochloric acid	0.7	0.7	1.0	0.4-0.5	0.25-1
Hydrofluoric acid	0.5	0.5	...	...	0.5-2
Nitric acid	1.0	1.0	3.0	...	0.1-0.2
Sulphuric acid	0.9	1.0	1.0	0.5-1.0	0.5-0.4
Calcium chloride	5.0	5.0	...	...	0.05-0.25 g.
Ammonium sulphate	10.0	10.0	...	...	0.05-0.25
Tannic acid	1.0	1.0	...	...	1.0
Oxalic acid	2.0	...	...	...	0.5-1.2
Tartaric acid	2.5	...	...	...	0.5-2
Citric acid	5.0	...	...	...	0.5-2

* Results embodied in Table III were done in collaboration with S. A. W. and V. V. K. S.

** References in this investigation are given of allied work of coagulation of the latices of *Manihot*, *Ficus*, *Kickxia*, *Castilla*, *Hancornia*, *Mascarenhasia*, *Lianas* (Vines), *Euphorbia*, *Jelutong* but with special reference to the work of *Hevea brasiliensis*.

When coagulation is effected with alkalis a minimum quantity of the reagent is necessary which would raise the p_n to 7.7. If the concentration is less there will be a partial coagulation and if it is more, the latex would turn into a pasty mass. In coagulation with alkalis there is an advantage that the process can be completed in a very short time but in the case of acids it is necessary to keep the latex overnight. The alkali coagulation has demerits as well. The coagulum is very spongy having a poor tensile strength and elasticity as compared to the coagulum obtained by acid coagulation. Further, the coagulum develops tackiness* and this depends further upon washing and temperature. If the coagulum is washed till it is free of its alkalinity and is dried at low temperature (70-80°), the tackiness becomes less. This faulty coagulation can be corrected to a great extent if the coagulum is dipped in an 1% solution of mineral and organic acids before washing.

With bases (quinoline, aniline, toluidine and pyridine) it was found that 0.2 to 1 c.c. of the base brought about effective coagulation of 10 c.c. latex. Smaller quantities of quinoline, aniline and toluidine could not be used owing to the immiscibility of the bases with water. It was studied with pyridine only and it was noticed that 1 c.c. of 0.5% solution of pyridine in tap water coagulated 10 c.c. of latex. The coagula emit an odour of the base which is not removed even on washing with water and alcohol. The p_n value of the serum obtained after coagulation with bases could not be determined but with 0.5% solution of pyridine there was a gradual increase from 4.6 to 5.4 on increasing the volume of coagulant from 1 c.c. to 10 c.c. In the case of alkalis it was pointed out that with increased alkalinity the latex turned into a pasty mass but with bases this behaviour was not noticed.

The action of acids and alkalis on latex shows that the latex has got a stability range from 4.2 to 7.5 or 7.7. At the extremes complete coagulation of the latex takes place but below 4.0 the latex passes into a second zone or phase. The findings that alkalis are to be avoided for coagulation find further support from a statement of Stevens and Stevens "As a rule caustic soda should be avoided for latex manipulation as under certain conditions the resulting rubber tends to soften and becomes tacky (sticky) due to some obscure type of chemical decomposition."

The salts can be used for the coagulation of latex and very small quantities are required. Good results were obtained with calcium and sodium chlorides, aluminium and ammonium sulphates and alum.

* Parkin, *Roy. Botn. Gard. Ceylon, Circ.* 1899, 1, 151.

Eaton, *Dept. Agr. Federated Malay States, Sp. Bull.*, 1912, 17, 25.

Zimmermann, "Dermanihot-Kautschuk," p. 250; G. Fischer, *Jrma*, 1913.

Ahrens, *Chem. Ztg.*, 1910, 35, 266.

Gorter, *Dep. Land. Nijverh. en Handel, Mededel. over Rubber*, 1912, 1, 4; 1912, 2, 201.

Henri, *Caoutchouc and Gutta percha*, 1910, 7, 4371.

P. Schidrowitz, "Rubber," 2nd. ed, 1916, p. 136.

O. de Vries, "Estate Rubber," p. 362.

Pohle, *Koll.-Chem. Beih.*, 1921, 13, 32.

Bamber, *Lectures on India Rubber*, by D. Spence, 1909, p. 201.

O. de Vries and Beunee-Nieuwland, *Arch. Rubber Cultuur*, 1927, 11, 567; 1925, 9, 760.

Stevens and Stevens, "Rubber Latex," 1940, p. 16.

Flint, "The Chemistry and Technology of Rubber Latex", 1938, p. 167.

Weber, *Gummi. Ztg.*, 1904, 19, 101.

A. W. de Jong and Tromp de Hass, *Ber.*, 1904, 37, 3301.

Special coagulants for proteins were also used and they also coagulated the latex but the concentrations used in the experiments were not very effective and the coagula produced by picric and tannic acids were coloured. Alcohol and acetone alone also brought coagulation and the same result was achieved by common dehydrating agents.

Formaldehyde, lemon juice, curd, molasses and serum itself coagulated the latex and so shortages of chemicals is no consideration in the coagulation of latex.

Water Coagulation.—Coagulation can be effected by adding latex to six volumes of hot water while five volumes brought about partial coagulation and four volumes produced flocculation. The dilution varies from season to season with percentage of rubber; it is less when the percentage of rubber is high and more when it is less especially during the defoliation period. p_H value also depends upon dilution. If cold water is added dropwise till a clear straw coloured serum is obtained, the p_H rises to 7.5 but coagulation can also be brought about at low p_H value when six or seven volumes of hot water are used.

Auto-coagulation and Auto-creaming.—When latex is allowed to stand quietly at room temperature (25-31°) for a day or two the suspended particles float to the surface leaving below a clear reddish brown serum. This stage is characterised by the fact that particles do not coalesce together and on stirring or shaking disperse again in the serum. At this stage it is possible to separate the flocculated mass from the serum which can be made richer in rubber content and the particles of which can be coalesced together by washing with water or by filtration. When the latex is allowed to stand for a week or so at room temperature, the particles of cream unite together and form a clot of rubber having a junket-like appearance. Both of these methods can be used for the coagulation of latex on a large scale. The p_H value drops from 4.6 to 4.2.

Coagulation by Heat.—Latex can be coagulated by natural heat or by artificial heat (dry heat, moist heat and smoking). This process will have an important bearing if the whole rubber is to be obtained from the latex.

Coagulation by Centrifuging and Shaking.—This method can be used on a large scale. The coagulum gets separated and floats to the surface. A part of the coagulum remains in the serum which can be recovered on dilution. The p_H value of the latex remains unchanged.

Coagulation by Electric Current.—When the current from a battery is passed through the latex, the rubber particles move towards the anode and thus carry a negative charge and produce a change in the hydrogen-ion concentration of the latex. Observed p_H was 3.8.

By the above methods the coagulation of the latex of *Gryptostegia grandiflora* can be brought about. Broadly speaking the methods can be divided into two classes: (i) Chemical method which involves the use of chemicals and which are added to the latex either from outside (coagulation by chemical reagents and water, coagulation by smoking) or which are formed within the latex due to changes brought about by enzymes, micro-organisms, electric current or due to some unknown cause (auto-coagulation and coagulation by electric current). It is noticed that the chemical process is always accompanied by a change in the hydrogen-ion concentration which ranges from 4.2 to 7.5. (ii) Physical method which does not involve the use of chemicals (coagulation by dry heat, by centrifuging and shaking) and no change is brought about in the hydrogen-ion concentration of the latex.

Explanations for the coagulation of latex will form part of a separate communication.

E X P E R I M E N T A L

Coagulation by Chemical Reagents

(a) *General Methods of Coagulation with Acids and Salts.*—The latex is taken in a beaker, and required quantity of the acid or the salt solution added and the mixture warmed at 90° for five minutes after keeping overnight at room temperature ($25-27^{\circ}$). The coagulum is separated, sheeted, washed well in running water, dried at $90-95^{\circ}$ and weighed. This dry rubber is known as D. R. C. (dry rubber content).

(b) *General Method of Coagulation with Alkalis* (*Current Sci.*, 1943, p. 255) *and Bases.*—The latex is taken in a beaker. On adding the required quantity of an alkali or an organic base the latex turns yellow or pink. The mixture is warmed for five minutes at 90° . On stirring with a glass rod a white coagulum and a clear yellow or reddish brown serum are obtained. The coagulum is sheeted and after washing well with water till it is free of alkalinity it is dried at $90-95^{\circ}$ in an air-oven.

(c) *Difference between the Coagula obtained by the above two Methods.*—In the case of coagula obtained by method (a) the fibres of rubber unite together and form a tough and tenacious close meshed network. The texture is hard to feel and takes some time to sheet it. Its tensile strength is great and has good elasticity. The coagulum obtained by method (b) is of a different nature altogether. It is a highly spongy mass in which the mesh is open and the fibres or threads do not form one compact tough structure. The coagulum can be spread enormously but is extremely poor in tensile strength. It breaks easily and has poor elasticity.

Correction of the faulty Coagulation.—If the coagulum obtained by method (b) is washed and is given a dip in 1 % solutions of hydrochloric, sulphuric and acetic acids for 15 minutes, it acquires a white colour and resumes the tensile strength and elasticity. Before drying it should be washed well with water. On drying tackiness still persists to a slight extent.

Coagulation by Acids

Preliminary observations showed that increased acidity, which would decrease the p_H value of the latex from 4.6 to 4.0, would also decrease its percentage of dry rubber content (D.R.C., 111). This inference helped in fixing the concentration of the acid solution and the following was the procedure adopted. Prepare a dilute solution of the acid, add in portions of 1 c.c. to latex (10 c.c.) and note the p_H value after each addition till it reaches 4.0. If 1 c.c. of any solution decreases the p_H to 4.0, the acidity was considered very high and it was reduced to such an extent that 4 or 5 c.c. would at least be required to lower the p_H to 4.0. With most of the acids 1 % solution was found effective for coagulating the latex but hydrochloric, sulphuric, nitric and boric acids gave good results with 0.25, 0.2, 0.2 and 0.1 % solutions respectively. After fixing the concentration of the acid solution its coagulating power was further studied by adding 1, 2, 3, 4, 5 and 6 c.c. to 6 portions of latex (10 c.c.) and determining the D.R.C. The concentration of the solution was then halved and likewise five more determinations of D.R.C. were made. The range of acidity of the two solutions helped in deciding the minimum and maximum quantity of the coagulant that would bring about effective coagulation of the latex. In the following tables for each observation 10 c.c. of the latex were used and white coagulum was obtained which could be sheeted and had good tensile strength and elasticity. The indicator used was bromocresol green unless otherwise mentioned. D.R.C. values throughout this investigation are compared with D.R.C. obtained by coagulating an equal volume of latex with water

because it coagulates the latex completely as mentioned elsewhere and will be shown in the tables as standard. The solutions of the acids were prepared in tap water. Results appear in Table II.

TABLE IIA

*Coagulating effect of inorganic acids**Hydrochloric acid*

Hydrochloric Acid (Whitby, *Agr. Bull., Fed. Malay States*, 1918, 6, 374) — With 0.5% solution two sets of experiments were done. In one the acid was mixed with latex and warmed in boiling water for 10 minutes and after keeping overnight was again warmed. In the second set the mixture was warmed only once after keeping overnight. It was found that warming after keeping overnight was better. In the first set of experiments there was flocculation but the flocks did not coalesce together. Experiments 1 and 2 gave coagula but in other cases increased acidity failed to produce any coagulum. From the second set it is clear that 1 c.c. of the acid solution containing 0.005 c.c. hydrochloric acid brought about coagulation of 10 c.c. latex to the extent of 94% and 0.025 c.c. acidity decreased it to 15%. Therefore the concentration of the acid solution was halved and 0.24% solution (2.5 c.c. concentrated acid in a litre of tap water) gave good results which showed that 0.025 c.c. of hydrochloric acid can bring about coagulation of 100 c.c. latex. In the case of Hevea the required acidity is 0.04–0.05%.

(a) With 0.5% solution. Mixture warmed before and after keeping overnight: (First set.)				(b) With 0.5% solution. Mixture warmed only once after keeping overnight: (Second set.)			(c) With 0.25% solution		
Vol. of coagulant in c.c.	Appearance of serum.	pH.	% of D.R.C. on vol. basis.	Appearance of serum.	pH.	% of D.R.C. on vol. basis.	Appearance of serum.	pH.	% of D.R.C. on vol. basis.
1	Milky	4.4	0.99	Turbid black	4.6	4.08	Dark and slightly turbid	4.4	4.76
2	"	4.3	1.03	"	4.4	3.97	"	4.3	4.68
3	"	4.2	0.53	Milky	4.3	0.30	"	4.2	4.15
4	"	4.1	0.82	"	4.2	0.51	Milky	4.1	0.88
5	"	4.0	0.65	"	4.0	0.66	"	4.0	—
6	"	3.9	—	—	—	—	—	—	—
Standard	—	—	—	"	—	4.46	—	—	4.91

Hydrobromic acid

(Best results are obtained with an acidity ranging from 0.005–0.003 c.c. per 20 c.c. latex.)

(a) With 1% solution.

(b) With 0.5% solution.

1	Clear, deep dark	4.5	4.36	Clear, deep dark	4.5	4.27
2	"	4.5	4.41	"	4.5	4.41
3	"	4.4	4.20	Turbid, deep dark	4.5	4.07
4	Turbid, deep dark	4.4	4.04	"	4.5	3.84
5	"	4.4	3.62	"	4.5	3.76
6	"	4.4	1.99	—	—	—
Standard	—	—	—	—	—	4.49

TABLE IIA (contd.)

Hydriodic acid

(Good reconéts are obtained with 0.005-0.030 c.c. acid per 10 c.c. latex.)

(a) With 1% solution.				(b) With 0.5% solution.		
Vol of coagulant in c.c.	Appearance of serum.	ρ_n	% D.R.C. on vol. basis.	Appearance of serum.	ρ_n	% D.R.C. on vol. basis.
1	Dark brown, turbid	4.4	2.12	Dark brown, turbid	4.4	4.50
2	"	4.2	2.07	"	4.4	4.37
3	"	4.0	1.50	"	4.3	4.32
4	Milky	—	—	"	4.3	4.34
5	—	—	—	"	4.2	4.13
Standard	—	—	—	—	—	4.49

Hydrofluoric acid

D. Sandmann, *Tropenpflanzer*, 1910, 14, 189. F. Frank, *Gummi Ztg.*, 1908, 22, 1404.
(0.005-0.02 c.c. coagulated 10 c.c. latex effectively.)

(a) With 1% solution.				(b) With 0.5% solution.		
1	Brownish red, turbid	4.4	6.83	Slightly milky	4.5	4.48
2	"	4.2	6.69	Brownish red	4.4	6.95
3	Milky	4.1	—	"	4.3	6.88
4	"	4.0	—	"	4.2	6.68
5	"	4.0	—	Milky	4.1	3.84
Standard	—	—	—	—	—	6.89

Sulphuric acid

J. L. Wiltshire, *J. Research Inst. Malaya*, 1932, 4, 94. H. Jumelle, "les Plantes a Caoutchouc et a Gutta", p. 335, (Paris, 1932).

(Coagulant 0.005-0.04 c.c. per 10 c.c. latex while in the case of Hevea the acidity is 0.05-1.0%.)

(a) With 0.2% solution.				(b) With 0.1% solution.		
1	Turbid, dark	4.4	4.57	Turbid, dark	4.4	3.94
2	"	4.3	4.54	"	4.4	3.90
3	Milky	4.2	0.97	"	4.3	3.33
4	"	4.0	0.15	"	4.3	3.17
5	"	—	0.15	"	4.2	4.46
Standard	—	—	—	—	—	4.91

Nitric acid

(Coagulation was best effected with an acidity 0.001-0.004 c.c. per 10 c.c. latex.)

(a) With 0.2% solution.				(b) With 0.1% solution.		
1	Turbid dark	4.3	3.75	Dark turbid	4.5	4.38
2	"	"	3.76	"	"	3.54
3	Milky	"	2.35	"	"	3.42
4	"	"	2.72	"	"	2.95
5	"	"	1.54	"	"	3.19
Standard	—	—	—	—	—	4.89

Syrupy phosphoric acid

(The range of acidity necessary for coagulation was 0.005-0.01 c.c. per 10 c.c. latex.)

(a) With 1% solution.				(b) With 0.5% solution.		
1	Turbid dark	4.1	4.18	Turbid dark	4.3	4.36
2	Milky	<4	2.14	"	4.2	4.43
3	"	"	1.20	"	—	4.30
4	"	"	0.11	Milky	—	0.24
5	"	"	0.07	"	—	0.16
Standard	—	—	—	—	—	4.49

TABLE IIA (contd.)

Boric acid

(0.005-0.02 g. acid coagulated 10 c.c. latex. This coagulant with further has the advantage of preserving the coagulum.)

Vol. of coagulant in. c. c.	(a) With 0.1% solution.			(b) With 0.5% solution.		
	Appearance of serum	pH	% of D.R.C. on vol. basis.	Appearance of serum.	pH	% of D.R.C. on vol. basis.
1	Turbid	4.6	5.49	Brownish red and turbid	4.6	6.89
2	"	"	6.57			6.78
3	Milky	to	3.27	"	to	6.81
4	"	"	4.67	"	"	6.50
5	"	4.4	2.47	"	4.4	5.75
Standard	—	—	—	—	—	5.15

Carbonic acid

[Air was blown by mouth into latex (10 c.c.) when a white coagulum and a very slightly turbid serum was obtained. The serum had pH 4.2. The coagulum after usual working weighed 0.2660 g. (2.66%) while the standard weighed 0.2750 g. (2.75%). W. Pahl., 'The Rubber Industry,' Ed. by J. Torrey and A. S. Wanders, p. 234, 1911. O. de Vries., 'Estate Rubber,' p. 187].

TABLE IIB

*Coagulating effect of organic acids.**Acetic acid*

[Stevens, *India Rubber J* 1955, 65, 521; Schdrowits and Goldsborough, *India Rubber World*, 1919, 44, 1147; Parkin, *India Rubber J.*, 1910, 40, 742; Crossbey, *ibid.*, 1911, 41, 1203; Morgan, "The Preparation of Plants Rubber," p. 58; "Plantation Rubber and Testing of Rubber," p. 44; Ultea, *Archief* 1217, 1, 407].

(0.1-0.4 c.c. of acid coagulated 200 c.c. of latex. Hevea latex requires 0.15-0.6% acidity.)

Vol. of coagu- lant in c.c.	Appearance of serum.	pH	% of D.R.C. on vol. basis.	Appearance of serum.	pH	% of D.R.C. on vol. basis.	Appearance of serum.	pH	% of D.R.C. on vol. basis.
(a) With 1% solution.				(b) With 0.5% soln.			(c) With 0.25% soln.		
1	Brownish red and turbid	4.4	5.46	Turbid	4.5	6.29	„	4.6	6.66
2	„	4.3	5.06	„	4.4	4.45	„	4.5	6.64
3	„	4.3	5.37	„	4.3	3.06	„	4.4	3.97
4	„	4.2	5.04	„	4.2	4.13	„	4.4	4.40
5	„	4.1	3.88	„	4.1	3.46	„	4.3	4.50
6	Milky	4.0	0.37	„	—	—	„	—	—
Standard	—	—	—	—	—	—	„	—	6.80

Oxalic acid

	(a) With 10% solution.			(b) With 0.5% solution.			(c) With 0.25% solution.		
1	Dark	4.1	1.74	Dark brown	4.3	2.14	Clear, dark	4.5	2.15
2	Milky	4.0	0.24	„ „	4.2	2.15	„ „	4.4	1.55
3	„	—	—	Milky	4.0	0.53	„ „	4.4	1.66
4	„	—	—	„	—	—	„ „	4.1	1.00
5	„	—	—	„	—	—	—	—	—
Standard	—	—	—	—	—	—	—	—	2.10

Results with acetic acid and oxalic acid solutions are presented in Table IIB. For mixtures with alcohol the following procedure was adopted. To latex (20 c.c.) were added 1 c.c. of 1% solution of acetic acid and 10 c.c. of alcohol drop by drop when there appeared a white coagulum and a reddish brown, turbid serum with p_n 4.6. The D.R.C. weighed 1.1986 g. (5.99%). Effect of alcohol was studied further. Observations are recorded in Table IIB.

Oxalic Acid, Acetic Acid and their Mixtures with Alcohol

In a previous communication (*J. Sci. Ind. Res.*, 1943, 2 365), it was pointed out that acetic acid failed to coagulate the latex. That remark was due to the fact that coagulant was not added with special reference to the hydrogen-ion concentration and the quantity of acid added exceeded the minimum quantity required to coagulate the latex and hence the latex passed into a second phase in which it became stabilised. The coagulation of the latex of the second stabilised phase has not yet been studied.

TABLE IIC

Acetic acid and alcohol mixture

(a) With constant vol. of alcohol.				(b) With increased vol. of alcohol.				
1% Acetic acid soln.	Alcohol.	Appearance of serum.	% of D.R.C. on vol. basis.	% Acetic acid soln.	Alcohol.	Appearance of serum.	p_n .	% of D.R.C. on vol. basis.
1	4	Turbid reddish brown	5.17	1	2	Turbid	4.5	2.30
2	4	"	4.62	2	4	"	4.5	3.12
3	4	"	4.38	3	6	"	4.4	5.56
4	4	"	3.10	3	8	"	4.4	5.92
5	—	—	—	4	10	"	4.4	6.18
6 standard	—	—	—	Standard	—	—	—	5.98

The latex mixed with the coagulants was left overnight; dilution with the alcohol gave latter results.

TABLE IID

Coagulation with organic acids

Vol. of Coagulant in c.c.	Appearance of serum	p_n	% D.R.C. on vol. basis	Appearance of serum	p_n	% D.R.C. on vol. basis
<i>Trichloroacetic acid</i>						
(0.01022-0.02044 g. was effective for coagulating 10 c.c. of latex).						
(a) With 1% solution.				(b) With 0.5% solution.		
1	Dark with slimy turbidity	4.3	5.37	Turbid	4.5	3.69
2	" " "	4.2	3.78	"	4.4	3.79
3	" " "	4.01	1.62	"	4.3	3.59
4	Thick, milky	—	0.53	"	4.3	4.20
5	" " "	—	0.55	"	4.2	3.84
6	" " "	—	0.32	—	—	—
Standard	—	—	—	—	—	4.93

TABLE IId (contd.)

Formic acid						
Coagulant.	Serum.	pH.	% D. R. C.	Serum.	pH.	% D. R. C.
[Spence, <i>India Rubber J.</i> , 1908, 425, Riehl, <i>Archief</i> , 1927 II, 354]. (Increased acidity decreased the percentage of rubber as observed in other cases. 0.03% Solution did not give good results)						

(a) With 1% solution.				(b) With 0.5% solution.			
1 c.c.	Turbid	4.5	7.10	Turbid	4.5	4.00	
2	"	—	6.79	"	—	4.21	
3	"	—	4.65	"	—	4.48	
4	Milky	—	2.66	Milky	—	2.47	
5	"	—	2.84	—	—	—	
Standard	—	—	6.99	—	—	5.00	

Butyric acid

(0.001—0.02 G. acid was found effective to coagulate 10 c.c. latex. Increased acidity stabilised the latex.)

(a) With 1% solution.			(b) With 0.5% solution.			
1	Dark and slimy turbidity	4.5	5.42	Dark and slimy turbidity	4.6	5.55
2	" " "	4.5	4.91	" " "	4.6	4.16
3	" " "	4.4	4.59	" " "	4.5	3.53
4	Milky	4.3	2.87	" " "	4.5	2.44
5	"	4.3	2.27	Milky	4.4	1.73
Standard	—	—	—	—	—	4.43

Tartaric acid

(0.01—0.03 G. acid coagulated 10 c.c. latex.)

(a) With 1% solution.			(b) With 0.5% solution			
1	Dark brown	4.4	2.19	Turbid dark	4.5	1.75
2	"	4.2	2.19	"	4.4	1.62
3	"	4.0	1.98	"	4.2	2.00
4	Milky	—	0.93	Milky	4.0	0.73
5	"	—	—	"	—	0.72
Standard	—	—	—	—	—	2.00

Lactic acid

(An acidity of 0.005—0.03 brought about coagulation of 10 c.c. latex.)

(a) With 1% solution.			(b) With 0.5% solution.			
1	Dark, slimy turbidity	4.4	5.52	Dark, slimy turbidity	4.5	4.22
2	" "	4.2	5.23	" "	4.4	3.32
3	" "	4.0	4.98	" "	4.3	3.44
4	" "	4.0	4.61	" "	4.2	3.93
5	Thick, milky	—	0.96	" "	4.1	4.42
6	" "	—	1.16	—	—	—
Standard	—	—	—	—	—	5.06

Citric acid

(0.005—0.03 G. of the acid coagulated 10 c.c. latex.)

(a) With 1% solution.			(b) With 0.5% solution.			
1	Turbid, dark	4.4	2.14	Turbid	4.5	2.18
2	"	4.2	2.22	"	4.4	1.87
3	"	4.0	2.00	"	4.2	1.71
4	"	—	1.97	"	4.0	1.71
5	"	—	1.75	"	—	1.53
6	"	—	1.15	—	—	—
Standard	—	—	—	—	—	2.10

Stabilisation of Latex or its passing to the Second Phase (Whitby, *Kolloid Z.*, 1913 12, 156; O. de Vries and Beumee-Nieuwland, *Arch. Rubber Cultuur*, 1926, 10, 503).—If acid is added to the latex which would drop the p_H value to 4.0 then the latex will remain milky and will not coagulate and will pass into the second phase or zone (*cf.* Hevea). Latex (100 c.c.) was mixed with 0.5 c.c. of hydrochloric, nitric and sulphuric acids in separate corked bottles. On keeping for three months no coagulation occurred. Cream particles floated to the surface of the serum but they redispersed on shaking.

Coagulation with alkalis and organic bases

Alkalis.—In every case test experiments were done with alkalis. The solution of the alkali was added dropwise to the latex with stirring and on slight warming till a white coagulum separated from a yellow or reddish brown serum.

Organic Bases.—Base was added to 10 c.c. latex when coagula were obtained which emitted an odour of the base and had brown streaks. The coagula were washed with water and finally with alcohol but still the smell of the base persisted. Due to the immiscibility of the bases with water smaller quantities of the bases were not used excepting pyridine.

TABLE III

Coagulating effect of alkali and organic bases

Vol. of coagulant.	Appearance of serum.	p_H .	% of D. R. C. on vol. basis	Vol. coagulant	Appearance of serum	p_H .	% of D. R. C. on vol. basis.
<i>Lime water</i>							
(For p_H values from 6.2 to 7.4 bromothymol blue and for 8.9 universal indicator were used)							
(a) With saturated lime water diluted in the ratio 10 : 19 (lime water : tap water).				(b) With saturated lime water diluted in the ratio 1 : 1 (lime water : tap water).			
10 c.c.	Milky	4.6	...	10 c.c.	Milky	5.2	2.23
20	"	4.8	...	20	"	6.2	2.40
30	"	5.0	3.04	30	...	...	...
Standard	...	...	3.89	Standard	...	...	2.90
(c) With saturated lime water at 31°, (N/25.5 approximately).				(d) Coagulant after mixing and warming gave a precipitate.††			
10	Dirty	7.1	2.50	10	Pinkish, dirty	...	1.85
20	Clear red	7.2	3.70	20	Clear red	7.4	3.26
30	...	...	...	30	" "	8.4	3.69
Standard	...	...	...	Standard	...	...	3.89

†† The percentage of the coagulum was reduced owing to the decrease in alkalinity.

Potassium hydroxide

(Bromothymol blue was used blue as indicator.)

(a) With N/20 solution.				(b) With N/20 solution.			
10	Dirty light pink	7.2	1.69	20	Clear red	7.7	3.50
Standard	...	...	2.90	30	"	...	3.30
				Standard	...	...	3.89

TABLE III (contd.)

Sodium carbonate

Coagulant.	Serum	<i>p</i> _H .	% D. R. C. (Bromothymol blue was used as an indicator)	Coagulant.	Serum.	<i>p</i> _H .	% D. R. C.
(a) With <i>N</i> /20 solution.				(b) With <i>N</i> 20 solution.			
10 c.c.	Dirty pink	6.5	1.69	30 c.c.	Clear red	7.7	3.65
20	" "	7.5	1.80	Standard	...	...	3.89
Standard	...	...	2.90				

*Sodium hydroxide**(Weber, *Ber.*, 1904 37, 3299. Bromothymol blue was used as an indicator).

10 of <i>N</i> /20 solution	Dirty pink	7.2	...	1 of <i>N</i> -soln.	Clear red	7.7	3.55
20 " "	Clear red	7.7	3.40	2.5 of <i>N</i> "	No coagulation, no separation of coagulation and serum on adding 2.5 c.c. more.		
20 of <i>N</i> /10 soln.	" "	7.7	3.67				

Slight variations in D. R. C. percentages are due to variation sampling.

Ammonium hydroxide

This is used for the preservation of Hevea latex. When added to the latex of *Cryptostegia* a big spongy clot of rubber separated which either turned black or developed black streaks on its upper surface and this observation pointed out that ammonia could as well be used as a coagulant.

(a) With 0.1% solution (0.1 c.c. of ammonia, in 100 c.c. water, *d* = 0.88.

(b) With 0.05% solution

1 c.c.	Turbid	...	4.98	1	Turbid	...	4.41
2	"	...	5.81	2	"	...	2.68*
3	"	...	3.10	3	"	...	5.72
4	"	...	5.36	Standard	"	...	5.34

* The variations in the percentage of the coagula are probably due to the escape of ammonia from the mixture on warming and keeping.

Quinoline

(1 c.c. weighed 1.032 g. The coagula had brown streaks.)

0.2 c.c.	Slightly turbid	...	7.66*	1.4	Slightly turbid	...	7.25
0.4	"	...	7.60	1.6	" "	...	7.06
0.8	"	...	7.61	2.5	" "	...	7.25
1.2	"	...	7.60	Standard	" "	...	6.56

* Variations may be due to washing and increased amount of the base which had no advantage.

Aniline(Pelizzola, *Giorn Di Chim. Ind. ed. Appl.* 6, p. 10.)

(1 c.c. weighed 1.021 g. The coagula were slightly coloured).

0.2 c.c.	Slightly turbid	...	6.90	1.4	Slightly turbid	...	6.67
0.6	"	...	7.05	4.8	" "	...	6.65
1.2	"	...	6.00	Standard	...	...	6.56

TABLE III (contd.)

Coagulant.	Serum.	p_H	% D.R.C.	Coagulant.	Serum.	p_H	% D.R.C.
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Aniline hydrochloride

The solution was prepared by dissolving 0.5 g. in 100 c.c. tap water. Small volume of 0.5% solution gave coagulum, but in most cases the serum remained milky. As this salt did not yield good results, salts of other bases were not used. (Th. Marx., *Tropenpflanzer*, 1912, 16, 92).

1 c.c.	Turbid	...	5.69	4 c.c.	Milky	...	Nil*
3	"	...	5.54	Standard	...	...	6.56

* Eleven experiments were done with the increased quantity of the coagulant, but none produced any coagulum after Expt. 3.

Toluidine

0.2	Slightly turbid	...	7.07	1.4	Slightly turbid	...	6.88
0.4	"	"	7.36	1.6	"	"	6.44
0.8	"	"	6.98	2.5	"	"	6.67
1.2	"	"	7.18	Standard	...	...	6.55

Pyridine

1 C.c. weighed 1.0206 g. The coagulum obtained from the bases (quinoline, aniline, toluidine and pyridine) is very spongy and can be sheeted enormously, but the texture is weak and has very little tensile strength as compared to the coagula obtained from acid coagulation. The experiments were performed by adding free base to the latex as well as by adding its solution in water. The coagula emitted pyridine smell and were white.

(a) With 1% solution.

0.2	Brownish red, turbid	...	6.52
0.6	"	"	6.60
1.0	"	"	6.46
1.4	"	"	6.70
2.0	"	"	6.86
Standard	...	...	6.56

(b) With 0.5% solution.

1	Turbid	4.6	5.30
3	"	4.9	5.28
5	"	5.0	4.95
9	"	5.3	4.89
10	"	5.4	5.24
Standard	...	...	4.89

Coagulation by Salts

Very dilute solutions of salts were used firstly because latex gets coagulated with tap water which contains only small quantities of dissolved substances and secondly because large quantities, if used and found useful, will not be available on account of shortage of chemicals due to war. The hydrogen-ion concentration values were helpful as a guide to the coagulation point when water, acids and alkalis were used as coagulants, but they led to no definite information with most of the solutions of the salts used for coagulating the latex in this investigation. Extremely weak solutions of sodium and calcium chlorides, aluminium and ammonium sulphate and alum gave good results. In all these experiments 0.1 and 0.05% solutions of the salts were used.

TABLE IV

Coagulating effects of various salts.

Vol. of coagulant.	Appearance of serum.	p_H .	% of D. R.C. on vol. basis	Appearance of serum.	p_H .	% of D. R. C. on vol. basis.
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Alum

Markley, *India Rubber Work*, 1908, 38, 401. H. P. Stevens, *R. G. A. Bull.* 1920, 2, 142.

(a) With 0.05% solution.

1	Turbid	4.6	6.82
2	"	"	7.13
3	Milky	10	4.89
4	"	"	5.09
5	"	4.7	5.79
Standard	—	—	—

(b) With 0.05 % solution.

Turbid	4.6	7.30
"	"	6.75
"	10	6.85
"	"	6.51
"	4.5	6.21
Standard	—	7.00

TABLE IV (contd.).

Coagulant.	Serum.	pH.	% D. R. C.	Serum.	pH.	% D.R.C.
<i>Aluminium sulphate</i>						
(a) With 0.1 % solution.				(b) With 0.05 % Solution.		
1 e.c.	Turbid	4.6	5.78	Turbid	4.6	6.90
2	"		4.12	"	to	7.30
3	"	to	3.40	"		6.38
4	"		3.90	"		6.25
5	"	4.5	3.40	"	4.5	6.31
Standard	—	—	—	—	—	7.00

Calcium chloride

A. Zimmermann, Pflanze 1911, 7, 409; G. Varnet, *Compt. rend.*, 1922, 175, 716;
Lindet, *ibid.*, 1922, 178, 798.

(a) With 0.1 % solution.				(b) With 0.05 % solution.		
1	Turbid	4.6	7.60	Turbid	4.6	8.09*
2	"		6.08	"		7.16
3	"		6.10	"	to	6.86
4	"	to	5.09	"	4.5	6.41
5	"		6.18	"	—	—
6	"	4.5	5.40	"	—	—
Standard	—	—	—	—	—	6.89

* Variations due to sampling. Sometimes cream comes on the top and if not properly shaken, will cause fluctuations in D. R. C.

Sodium chloride

(a) With 0.1 % solution.				(b) With 0.05 % solution.		
1	Milky	4.5	3.79	Turbid	4.5	7.15
2	Turbid	"	6.32	"	"	6.68
3	"	"	6.03	"	"	5.97
4	"	"	5.94	"	"	6.18
5	"	"	6.10	—	—	—
Standard	—	—	—	—	—	—

Ammonium sulphate

(a) With 0.1 % solution.				(b) With 0.05 % solution.		
1	Turbid	4.5	6.40	Turbid	4.5	6.21
2	"	"	6.24	"	"	5.78
3	"	"	5.16	"	"	6.40
4	"	"	5.99	"	"	5.80
5	"	"	5.71	"	"	6.01
Standard	—	—	—	—	—	6.89

Aluminium chloride

(a) With 0.1 % solution.				(b) With 0.05 % solution.		
1	Turbid	4.4	6.08	Milky	4.5	3.51
2	"		4.74	"		3.52
3	"		3.98	Turbid	"	5.53
4	"	to	4.04	"	"	5.07
5	Milky		1.50	"	"	4.84
6	"	4.3	2.71	—	—	—
Standard	—	—	—	—	—	6.89

TABLE IV (contd.)

Coagulant.	Serum.	f_{R} .	% D. R. C.	Serum.	f_{R} .	% D. R. C.
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Mercuric chloride

Lecompte, Ind. Rubber J., 1913, 48, 19.

(a) With 0.1% solution.				(b) With 0.05% solution.		
1 c.c.	Turbid	4.5	6.19	Thick, milky	4.5	3.96
2	Thick, milky	"	2.38	"	"	2.80
3	"	"	1.25	"	"	1.52
4	"	"	1.13	"	"	1.92
5	"	"	0.88	—	—	—
Standard	—	—	—	—	—	6.89

Nickel sulphate

(a) With 0.1% solution.				(b) With 0.05% solution.		
1	Turbid	4.5	5.94	Turbid	4.5	4.65
2	"	"	5.65	"	"	5.67
3	"	"	5.38	Milky	"	3.23
4	"	"	4.20	"	"	1.70
5	Milky	"	3.00	—	—	—
Standard	—	—	—	—	—	6.89

Cobalt nitrate

(a) With 0.1% solution.				(b) With 0.05% solution.		
1	Milky	4.5	3.78	Milky	4.5	3.05
2	"	"	3.10	"	"	3.90
3	"	to	3.84	"	"	4.25
4	"	"	2.99	"	to	4.88
5	"	"	3.83	"	4.4	3.37
6	"	4.4	3.93	—	—	—
Standard	—	—	—	—	—	6.89

Lead acetate

(a) With 0.1% solution.				(b) With 0.05% solution.		
1	Turbid	4.5	4.28	Turbid	4.5	5.14
2	Milky	"	3.50	Milky	"	3.55
3	"	"	3.94	"	"	4.70
4	"	to	3.96	"	"	2.26
5	"	"	2.94	"	"	3.06
6	"	4.3	3.52	"	"	—
Standard	—	—	—	—	—	6.89

Copper sulphate

(Coagulum was brownish.)

(a) With 0.1% solution.				(b) With 0.05% solution.		
1	Turbid	4.4	6.40	Turbid	4.4	5.58
2	"	"	6.41	"	"	5.63
3	"	to	5.05	"	to	5.86
4	"	"	4.59	"	"	5.58
5	"	"	2.03	"	4.3	3.49
6	"	4.3	3.59	—	—	—
Standard	—	—	—	—	—	6.89

TABLE IV (contd.)

<i>Zinc chloride</i>						
(a) With 0.1% solution.				(b) With 0.05% solution.		
Coagulant.	Serum.	pH.	%D.R.C.	Serum.	pH.	%D.R.C.
1 c.c.	Milky	4.5	4.72	Milky	4.5	3.91
2	"	"	3.63	"	"	5.82
3	"	"	2.32	"	"	2.52
4	"	"	3.35	"	"	2.67
5	"	"	2.71	"	"	3.70
6	"	"	2.97	"	"	—
Standard	—	—	—	—	—	6.38

<i>Manganese sulphate</i>						
(a) With 0.1% solution.				(b) With 0.05% solution.		
1	Turbid	4.5	7.53	Turbid	4.5	7.37
2	"	"	5.52	"	"	7.41
3	"	"	4.95	"	"	7.03
4	"	"	5.01	"	"	6.78
5	"	"	4.99	"	"	6.86
6	Milky	"	3.52	—	—	—
Standard	—	—	—	—	—	7.89

<i>Potassium ferrocyanide</i>						
(a) With 0.1% solution.				(b) With 0.05% solution.		
1	Slightly turbid	4.5	7.12	Turbid	4.5	5.62
2	"	"	7.22	"	"	5.76
3	Milky	"	1.80	"	"	6.05
4	"	"	1.44	"	"	5.71
5	"	"	1.98	"	"	5.22
Standard	—	—	—	—	—	7.89

<i>Potassium fericyanide</i>						
(a) With 0.1% solution.				(b) With 0.05% solution.		
1	Turbid	4.5	7.35	Turbid	4.5	8.21
2	"	"	7.13	"	"	7.01
3	"	"	4.53	"	"	6.12
4	Milky	"	3.56	"	"	7.38
5	"	"	3.76	"	"	5.21
Standard	—	—	—	—	—	7.89

<i>Sodium Stillofluoride</i>						
(a) With 0.1% solution.				(b) With 0.05% solution.		
1	Milky	—	4.80	Turbid	—	5.87†
2	"	—	2.30	Milky	—	2.73
3	"	—	1.50	"	—	3.21
4	"	—	2.55	"	—	2.11
5	"	—	1.97	"	—	3.61
Standard	—	—	1.92	—	—	7.89

† It appears that still lesser quantities of the coagulant will give better results.

Coagulation and Hydration.—Alcohol was used under this head and the details are given under reagents used for coagulating proteins.

Coagulation and Dehydration.—Anhydrous potassium carbonate, anhydrous sodium sulphate, sodium and potassium hydroxides, phosphorus pentoxide and zinc chloride were used. In every case 1 g. of the reagent was added to 10 c.c. of latex. Good and white coagulum was obtained with anhydrous sodium sulphate and zinc chloride, while a coloured coagulum was obtained with potassium carbonate. With potassium and sodium hydroxides pasty masses were produced. Phosphorus pentoxide thickened the latex.

Protein Coagulating Reagents. *Alcohol* (O. de Vries and Beumee-Nieuwland, *Arch. Rubber Culture*, 1927, 11, 518).—58% Alcohol was gradually added dropwise to latex (20 c.c.) when on adding 11 c.c. a white coagulum and a turbid brownish red serum were obtained. The coagulum after sheeting weighed 1.2430 g. or 6.22%. The turbidity of the serum persisted even after adding a further volume of 13 c.c. of alcohol and appears to be due to the coagulated and separated proteins, etc. The p_H of the serum remained unchanged (4.6). Thus the volume of alcohol required to coagulate the latex is half the volume of latex taken for coagulation.

Acetone.—Acetone was added dropwise from a burette to latex (10 c.c.) when on adding 10 c.c. a white coagulum and a brownish red serum were obtained. The p_H value remained unchanged (Weber, *Ber.*, 1903, 36, 3110; Schidrowitz and Kaye, *India Rubber J.*, 1907, 34, 377).

Besides alcohol and acetone, picric, tannic, phosphotungstic acids were used for the coagulation of latex. The quantities of coagulants required to coagulate 10 c.c. latex were 0.05–0.1; 0.05–0.2; and 0.025–0.05 g. respectively. The coagulum from picric acid was yellow and from tannic acid violet, but it was white from phosphotungstic acid.

TABLE V

Coagulating effect of protein precipitating and miscellaneous reagents

Vol. of coagulant.	Appearance of serum.	p_H	% of D.R.C. on vol. basis.	Appearance of serum	p_H	% of D.R.C. on vol. basis.
<i>Picric acid</i>						
(a) With 1% solution.				(b) With 0.5% solution.		
1	Clear yellow	4.4	2.17	Clear yellow	4.5	2.17
2	Turbid yellow	4.2	1.70	"	4.4	3.00
3	Deep yellow flocculation	4.2	—	Yellow flocculation	4.4	1.62
4	" "	4.0	—	" "	4.3	0.37
5	" "	—	—	" "	4.3	—
Standard	" "	—	2.00	" "	—	4.49

Tannic acid

Eaton, *Dept. Agr. Federated Malay States, Sp. Bull.*, 1912, No. 17, 17.

(a) With 1% solution.				(b) With 0.5% solution.		
1	Dark violet, turbid	4.5	2.26	Dark violet, turbid	4.5	1.96
2	" " "		2.05	" " "		2.10
3	" " "	to	1.89	" " "	to	1.82
4	" " Flocculation		0.43	" " "		1.12
5	" " "	4.3	0.68	" " "	4.4	1.05
Standard	" " "	—	—	" " "	—	2.00*

* Latex was received at different intervals of time and hence the fluctuations in D. R. C.

TABLE V (contd.)

Phosphotungstic acid

Vol of coagulant.	Appearance of serum.	p_H	% of D.R.C. on vol. basis	Vol. of coagulant	Appearance of serum	p_H	% of D.R.C. on vol. basis.
(a) With 1% solution.				(b) With 0.5% solution.			
1 c.c.	Flocculation	4.6	0.06		Dark Turbid	4.6	2.27
2	"	4.5	0.21		"	—	2.24
3	Turbid	4.4	2.25		"	—	1.32
4	"	4.3	3.00		"	—	1.89
5	"	4.3	3.47		"	—	2.20
Standard		—	—			—	4.49

To latex (10 c.c.) was added with stirring 40 per cent formalin in portion of 0.1 c.c. A small pellet of rubber formed when 0.5 c.c. of the solution was added. Complete coagulation did not take place even after adding 1 c.c. but the latex thickened. On diluting the mixture with 50 c.c. water, flocculation occurred and the flocks formed the surface layer leaving below a clear layer of serum. On stirring, the flocks redistributed but did not coalesce together but stuck together after collection on a filter bed. The filtered mass was washed and dried in an air oven at 90-95° and weighed 0.5300 g. (5.30%). There was no change in the hydrogen-ion concentration of the serum before dilution. When this experiment failed, lesser concentrations were used and the results show that very dilute solutions of formaldehyde can bring about coagulation.

Formaldehyde

(a) With 0.1% solution.				(b) With 0.05% solution.			
1	Brownish, turbid	—	7.03		Brownish, turbid	—	6.80
2	"	—	6.36		"	—	7.12
3	Milky, turbid	—	2.73		"	—	6.64
4	"	—	1.12		"	—	6.02
5	"	—	1.32		"	—	1.58
Standard		—	—			—	6.89

Serum

Serum was added to latex and the mixture was kept in boiling water for 15 minutes but no change occurred in the p_H value. The results show that an increase in the volume of serum decreased the percentage of coagulum and accordingly lesser quantities of serum were used and gave better results.

5	Milky	4.6	5.02	2.5	Turbid	—	6.69
10	"	"	3.74	3.0	"	—	5.89
20	"	"	0.10	3.5	"	—	6.36
0.5	Turbid	—	6.89	4.0	"	—	5.78
1.0	"	—	6.85	4.5	"	—	6.06
1.5	"	—	7.21	5.0	"	—	6.60
2.0	"	—	7.27	5.5	"	—	5.43
				Standard	—	—	6.89

*Lemon juice.**—(Wildeman, *J. L'Agrie. Trop.*, 1905, 347) Latex (50 c.c.) was mixed with lemon juice (2 c.c.) which on keeping for 24 hours thickened but did not separate a coagulum, but on slight warming coagulated and the p_H value decreased from 5.0 to 4.5. The serum coagulated two further quantities of the latex.

*Curd.**—Sour curd was strained through muslin and 1 c.c. of this was added to latex (50 c.c.) The mixture thickened on keeping overnight and on stirring and gentle warming on the water.

* Note the p_H of latex and that of serum. The latex for these experiments was obtained last winter (January 1943).

bath separated into a coagulum and serum. The p_H dropped from 5.0 to 4.7. The serum coagulated two fresh quantities of latex more.

Molasses.—Thick molasses (2 c.c.) was added to latex (50 c.c.). On keeping overnight no change occurred in the consistency of the mixture but after stirring and warming on the water-bath for 15 minutes, the coagulum separated and the p_H value dropped from 5.0 to 4.5.

Coagulation by Addition of Water

Water was gradually added dropwise to latex (50 c.c.) and on addition of 20 volumes of water (1,000 c.c.) flocculation took place and the particles coalesced together to form a jelly-like spongy mass leaving behind a clear straw-coloured serum. The gelatinous mass on squeezing, pressing and washing formed a membrane which turned transparent on dehydration at 100°. The p_H values for distilled water, latex and serum were 7.0, 5.0 and 6.2 respectively. Latex of *C. grandiflora* can be coagulated with distilled water. (Dubosc and Luttringer, "Rubber: Its Production, Chemistry and Synthesis" Eng. Ed. by E. W. Lewis, 1918, p. 127; Siddiqui *et al.*, *loc. cit.*).

The same behaviour is noticed by using tap water; 12 to 16 volumes are necessary for complete coagulation and p_H values for tap water, latex and serum were 7.5, 5.0 and 7.5 respectively. But when the latex was diluted with water and warmed to 80–90°, the dilution was reduced to 8–10 volumes. If latex is added to boiling water, then the volume is further reduced to 6 and D.R.C. percentages of 3.8 and 3.5 were obtained when latex (10 c.c.) was coagulated with tap water (200 c.c. and 60 c.c. respectively), 5 volumes brought about partial coagulation while 4 volumes of water produced flocculation and the flocks did not agglomerate together even on keeping in boiling water but stuck together when collected on a filter and washed.

Fresh and saline waters from the Estate (Imperial Agricultural Research Institute Area) and river and canal waters were used and similar results were obtained. It may be pointed out that salinity decreased the extent of dilution while cold and ice-cold water had no advantage.

In the light of results of laboratory experience, the water coagulation method was developed and submitted to semi-large scale trials. A quantity of latex (6.5 lbs. was diluted with hot water ten times). The latex set to a spongy mass which formed a sheet $6\frac{1}{2} \times 4\frac{1}{2} \times 7\frac{1}{8}$ inches weighing 5½ oz.

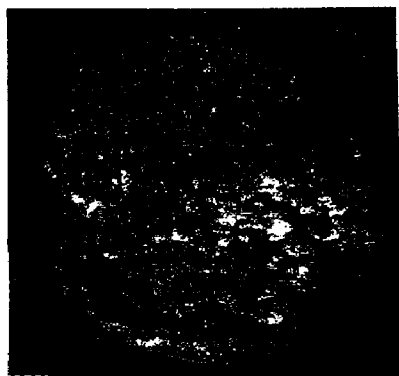
Formation of a Black Substance on Coagulation with Water.—When latex is coagulated with water and the coagulum and serum are allowed to stand overnight a black substance is formed over the coagulum as well as the serum. The liquid obtained from the pressings of the coagulum is also rich in it. (O. de Vries, "Estate Rubber" p. 30.) The black substance once developed on the coagulum is not removed on washing with water or acidulated water. Investigations on the cause of this revealed that alkalinity helps the formation of this black substance and acidity retards it (Zimmermann, *Pflanzer*, 1910, 6, 117; D. Spence, *Gummi Ztg.* 1910, 22, 1375). The coagulum after sheeting and washing if dipped for 15 minutes in 0.05% solution (acid 0.05 c.c. in tap water 100 c.c.) of hydrochloric, sulphuric and nitric acids remains white and can be kept under water exposed to the air without change in colour. The best results were obtained with nitric acid. The water is to be changed from day to day, otherwise it will develop a foul smell and bacteria. A sheet of rubber was kept immersed in water for two months after this treatment it remained white.

If the sheet is partially immersed in water, the portion exposed to the air becomes violet, brown and finally deepens in colour.

Auto-coagulation

When latex is allowed to stand for a few days at room temperature (28-30°) auto-coagulation results with the separation of a white spongy clot of rubber and a clear reddish brown serum having p_H value 4.2. In a previous communication (*J. Sci. Ind. Res.*, 1943, 2, 357) the p_H was recorded as 4.6. The difference in acidity due to seasonal variations may be responsible for this). The coagulum when pressed into gool sheets (Fig. 1) has good tensile strength and elasticity and does not show any properties of deterioration or decomposition. The auto-coagulation appears to be due to the changes of decomposition brought about by enzymes, etc. present in the latex. An increase in the acidity and a shift of p_H value from 4.6 to 4.2 further confirms this observation. In some cases when the latex is allowed to stand quietly in uncorked bottles, the surface of latex turns violet-brown and finally black and on it develop moulds with a yellowish colour. The same moulds developed in the serum when it was exposed to air and were identified as (a) *Aspergillus flavus ovyzae* and (b) *Aspergillus niger van Teighen*. A sheet of undried rubber when kept in water without changing it and exposed to the air developed a foul smell and the examination showed bacteria (Vernet, *Bull. Marseille*, 1919, 1, 118) and spores of saprophytic fungus like *Cladosperring Sp.* etc. Thus the change in auto-coagulation can be attributed to the action of enzymes, micro-organisms and also to some other unknown causes. (Gorter and Swart, *Meded. Rubber Profsta, Java* No. 6; D. spence, *Lectures on India Rubber*, 1909, 198).

FIG. 1



Auto-creaming.—When the latex is allowed to stand for a day or two its cream or suspended particles float to the surface leaving below a clear serum which can be syphoned off by a rubber tubing. The cream on separation forms a big clot of a spongy mass on dilution or washing with water. The cream also sticks by the agglomeration of particles when collected on a filter. This method is of practical importance and can be recommended for the coagulation of rubber and has the advantage that it requires less dilution for the coalescence of the rubber particles and also eliminates big coagulating equipment. (Flint, "The Chemistry and Technology of Rubber Latex" 1938, p. 167). The only necessary thing is to find a preservative so that it may not develop any bad smell due to decomposition on keeping, or when transported from place to place. This work will form part of a separate communication.

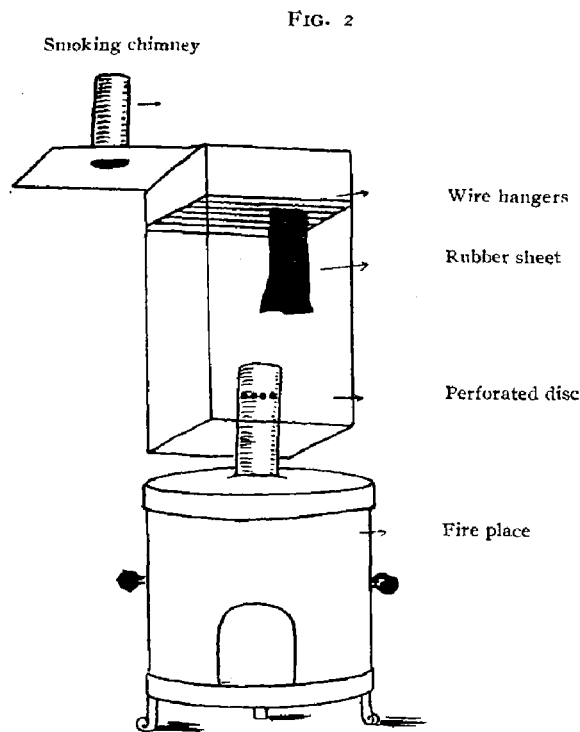
Coagulation by Heat

Natural Heat.—When a twig is cut the latex at the cut end dries up and forms a seal which can be pulled and the latex that flows down coagulates on the ground. Similarly when

the whip is scratched by a knife or a needle the small drops of latex ooze out and dry on it in small globules. These are examples of coagulation due to natural heat.

(b) *Artificial Heat. Dry Heat.*—When latex (10 c.c.) is warmed on a sand or water-bath, it begins to form a thin film or membrane on the upper surface of the latex at about 50° , then thickens and gradual and complete coagulation takes place at about $80-84^{\circ}$ leaving a little brown serum (Duboc, and Luttringer, *loc. cit.*, p. 122). The p_H value of the latex remained unchanged (4.6). This process is important when whole rubber is required.

Smoking.—When latex is exposed to the action of smoke then it gets concentrated



and impregnated with smoke acids and cresote oil etc. The impregnation of the latex causes its coagulation. (Dominikos, *Gummi Ztg.* 1908, 22, 926; G. Waldrom, *India Rubber World*, 1906, 30, 188). A smoking chamber designed in this laboratory is shown in Fig. 2. It consists of a fire place and an upper chamber provided with a chimney and the arrangement for hanging rubber sheets. At the bottom the chamber is connected with the fire place with a perforated disc through which the smoke enters from the fire place to the upper chamber. The paddy husk was used in the fire place for producing smoke. Rubber sheets were also dried in this smoking chamber and suffered a loss of 31 and 17% on drying in three hours' time. The less moisture content in the second sheet may be due to good pressing. The sheet after drying appears to have properties of cured rubber and a strip cut from the sheet

can be pulled four to five times its size and has a very good tensile strength and elasticity.

Moist Heat or Steam.—Steam was passed in a beaker containing latex (20 c.c.) for three minutes till the volume increased to 30 c.c. when a white coagulum and a turbid serum were obtained. The experiment was repeated thrice. The coagula after washing and drying at $90-95^{\circ}$ gave 6.67, 5.90, 6.0%.

Coagulation by Centrifuging and Mechanical Shaking

Shaking.—Latex (10 c.c.) was shaken in a corked test tube till it separated into a coagulum and a clear straw coloured serum. The p_H value of the latex remained unchanged.

The D.R.C. amounted to 2.47% which was comparable to the percentage obtained by coagulating an equal volume of latex with water.

Centrifuging.—Latex (10 c.c.) was centrifuged in a rapidly rotating centrifuge when coagulum separated as a hard disc or button and came to the top within ten minutes. (D.R.C. % of 4 observations were 5.5, 6.2, 6.3, 6.6). The serum was turbid and on dilution with water yielded a further quantity of coagulum. (D.R.C.% of 4 observations were 1.0, 0.6, 0.5 and 0.2). The p_H of the latex remained unchanged. This process can be used for the coagulation of latex on a large scale. (Biffen, *Kew Bull. Misc. Information*, 1890, 179).

Separation of Coagulum from the Latex by Alpha-Alpha Separator.—A litre of latex was churned when a clear serum was obtained on feeding the latex a number of times. The coagulum stuck to the internal spherical balls and clogged the machine. The whole operation of the separation of coagulum was completed in ten minutes. This is also suggestive of the fact that a centrifuge used for sugar could be used for the separation of rubber from the latex on a large scale.

Coagulation by Electric Current

Current was passed through latex diluted with water by using copper electrodes when flocculation occurred but a clear serum was not obtained. The whole mass became dirty yellow and finally on keeping turned black. With carbon electrodes the serum as well as the coagulum did not turn black on passing the current. Finally the current was passed in a U-tube with platinum electrodes when the dispersed particles began to move towards the anode and bubbles began to come out copiously at the cathode at which there was also deposition of a substance which first turned yellow and finally from brown to black. The deposited matter at the anode even after keeping for a week remained white and came to the top in the limb of the U-tube leaving the clear serum below. The experiment indicates the charge carried by the dispersed particles of the latex to be negative. The p_H value of the serum was 3.8 and so the change is a chemical one brought about by the changes of decomposition which resulted in increased acidity of the serum. (*India Rubber World*, 1926, 75, 127; *Trans. Inst. Rubber Ind.*, 1928, 4, 343).

Stages of Coagulation. (Beadle and Steverfs, *Kolloid, Z.*, 1913, 13, 217).

1. *Formation and Separation of Cream.*—The latex is allowed to stand quietly at room temperature (25-31°) or when it is diluted with water (4 volumes) the fine suspended particles of latex slowly separate out and begin to float to the surface. If the liquid is stirred the particles again mix with the serum and redistribute uniformly to make it latex.

2. *Separation of Latex into Cream and clear Serum.*—The fine white particles of cream in (1) further agglomerate together and form bigger particles of cream and collect on the surface forming an upper surface of cream and lower layer of clear serum. The cream can be redistributed and separated by filtration.

3. *Coagulation.*—The upper white cream on touching with a glass rod forms a voluminous spongy and jelly-like mass due to the formation of a net-work of rubber threads and fibres by their crossings and recrossings and the whole clot can be lifted bodily from the serum. At this stage when the fine fibres or threads of rubber unite together they are no more particles of cream which can be redistributed in the serum on shaking or stirring. The cause has not been examined but it is probable that the change is brought about by the disruption of electrical and molecular cohesive forces.

Confirmation of the Results of Coagulation on a Semi-large Scale

The following coagulants were used to coagulate 1 pound of latex of *C. grandiflora* in order to confirm the results obtained by coagulating 10 c.c. of the latex. The following observations confirm the previous findings.

TABLE VI

Percentages of D.R.C. from 1 lb. latex

No.	Name of the coagulant.	Amount of the coagulant.	Vol. of water in which the coagulant was dissolved.	Wt. of D.R.C.	% of D.R.C. on wt. basis.
1	Hydrochloric acid	0.1075 c.c.	43 c.c.	24.69 g.	5.74
2	Nitric acid	0.043	43	23.76	5.54
3	Acetic acid	0.43	43	26.93	6.26
4	Sulphuric acid	0.172	43	28.59	6.65
5	Sodium hydroxide	0.43 g.	43	28.38	6.60
6	Ammonia (conc.)	0.86 c.c.	—	23.05	5.36
7	Pyridine	0.516	50	28.19	6.56

Cost of Coagulation.—Table VII shows the quantity of latex in lbs. which can be coagulated by one pound of the coagulant and its cost at present and pre-war rates and also the cost of coagulation of $9\frac{3}{4}$ tons of latex at present and pre war rates.

TABLE VII

Cost of coagulation

Name of coagulant.	Quantity of latex coagulated by 1 lb of coagulant.	Price of coagulant.		Cost of coagulation of $9\frac{3}{4}$ tons of latex.			
		Pre-war rates.	Present rates.	Pre-war rates.	Present rates.	Pre-war rates.	Present rates.
		RS. AS. P.	RS. AS. P.	RS. AS. P.	RS. AS. P.	RS. AS. P.	RS. AS. P.
Hydrochloric acid	3800 lbs.	0 0 6	0 14 0	0 3 0		5 2 6	
Sulphuric acid	1500	0 1 1	2 4 0	0 15 6		32 4 0	
Nitric acid	9250	0 0 4	3 4 0	0 1 0		11 6 0	
Sodium hydroxide	269	0 4 0	1 0 0	20 0 0		80 0 0	
Boric acid	21500	0 5 6	3 8 0	0 5 6		3 8 0	
Oxalic acid	2150	0 8 0	2 12 0	6 0 0		27 8 0	
Citric acid	2150	1 2 0	12 8 0	11 4 0		125 0 0	
Calcium chloride	21500	1 7 0	2 12 0	1 7 0		2 12 0	
Sodium chloride	21500	0 10 0	1 2 0	0 10 0		1 2 0	
Ammonium sulphate	21500	0 8 0	1 4 0	0 8 0		1 4 0	
Aluminium sulphate	21500	1 6 0	5 8 0	1 6 0		5 8 0	
Alum	21500	1 4 0	5 14 0	1 4 0		5 14 0	
Acetic acid	200	0 10 0	3 15 0	67 3 0		416 0 0	
Formic acid	300	1 10 0		116 7 0			

TABLE VIII

Coagulating effect of various substances ††

Quantities of coagulants in g. or c.c. and water of dilution per litre of 2.7 %
Latex of *Cryptostegia grandiflora*.

Name of coagulant.	Coagulant in g. or c.c./litre		Vol. of water* in which the coagulant was dissolved	
	Minimum.	Maximum.	Minimum.	Maximum.
1. Hydrochloric acid	0.25 c.c.	1.0 c.c.	100 c.c.	400 c.c.
2. Hydrobromic acid	0.50	3.0	100	600
3. Hydroiodic acid	0.50	3.0	100	600
4. Hydrofluoric acid	0.50	2.0	100	400
5. Sulphuric acid	0.40	0.5	100	200
6. Nitric acid	0.10	0.2	100	200
7. Phosphoric acid (syrupy)	0.5	1.0	100	200
8. Boric acid	0.05 g.	0.3 g.	100	600
9. Acetic acid	0.25 c.c.	4.0 c.c.	100	400
10. Trichloroacetic acid	0.5 g.	2.0 g.	100	400
11. Formic acid	0.25 c.c.	2.0 c.c.	100	400
12. Butyric acid	0.5	3.0	100	600
13. Tartaric acid	0.5 g.	1.2 g.	100	400
14. Lactic acid	1.0 c.c.	3.0 c.c.	100	600
15. Oxalic acid	0.5 g.	1.2 g.	100	300
16. Citric acid	0.5	2.0	100	400
17. Lime water	1000 c.c. of N/25.5 solution		...	...
18. Potassium hydroxide ‡	5.6 g.	5.6 g.	...	...
19. Sodium carbonate ‡	11.0	11.0	...	...
20. Sodium hydroxide ‡	4.0	4.0	...	...
21. Quinoline †	20 c.c.	...	...	...
22. Aniline †	20.0	...	...	...
23. Toluidine †	20.0	...	...	...
24. Pyridine	0.5	2.0	100	400
25. Alum	0.05 g.	0.25	100	500
26. Aluminium sulphate	0.05	0.25	100	500
27. Calcium chloride	0.05	0.25	100	500
28. Sodium chloride	0.05	0.20.	100	400
29. Ammonium sulphate	0.05	0.25	100	500
30. Aluminium chloride **	0.1	0.1	100	...
31. Mercuric chloride **	0.1	0.1	100	...
32. Nickel sulphate **	0.1	0.1	100	...
33. Cobalt nitrate **	0.2	0.2	200	...
34. Lead acetate	0.05	0.05	100	...
35. Copper sulphate	0.05	0.20	100	...
36. Zinc chloride **	0.1	0.1	100	...
37. Manganese sulphate	0.05	0.25	100	500
38. Potassium ferrocyanide	0.05	0.15	100	300
39. Potassium ferricyanide	0.05	0.20	100	400
40. Sodium silicofluoride	0.05	0.05	100	...
41. Picric acid **	1.0	1.0	100	...
42. Tannic acid **	1.0	1.0	100	...
43. Lemon juice	40.0 c.c.	40.0 c.c.	...	...
44. Curd	20.0	20.0	...	...
45. Water	6000	12000	...	...
46. Formalin	0.05	0.2	100	400
47. Alcohol (98 %)	555.0	555.0	...	...
48. Acetone	1000.0	1000	...	...

* No definite rule can be fixed for the minimum and maximum dilution. A concentrated solution would require lesser dilution. The table embodies the results of dilution found effective in this investigation.

‡ Dilution would depend upon the normality of the solution e.g. 1000 c.c. lime water of N/25.5 strength are required to coagulate 1 litre of latex while only 10 c.c. of 10 N-sodium hydroxide solution were effective

† Minimum and maximum quantities of the bases were not determined due to their immiscibility in water.

** Substances were not good coagulants in the concentrations used.

†† Coagulation studies embodied in this investigation were done mostly on latex having pH 4.6 and collected from Okhla plantations, Delhi, during the months of August and September, 1943 and it was noticed that seasonal variations of temperature and time exercise a great effect in bringing about coagulation. Low temperature of winter months has a retarding effect while that of summer is favourable for it.

Practical Recommendations

The coagulation of *Cryptostegia grandiflora* latex can be brought about effectively by the following methods. The quantity of the coagulants required to coagulate one litre of latex are given in Table VIII and the details of the method in the experimental portion.

1. Water coagulation method.
2. Auto-coagulation method.
3. Auto-creaming method.
4. Coagulation by chemical reagents.
 - (a) By mineral and organic acids.
 - (b) By alkalis and pyridine.
 - (c) Salts: sodium and calcium chlorides, aluminium and ammonium sulphates and alum.

C O N C L U S I O N S

1. Coagulation can be brought about by methods which are physical and chemical in nature. The chemical methods are suitable for the coagulation of latex on a large scale.
2. The latex coagulates at a p_H range from 4.2-7.5.
3. The range towards p_H 4.2 is reached by acids and acid salts.
5. Coagulation when effected by chemical reagents, by auto-coagulation or by passing electric current is always accompanied by a change in the hydrogen-ion concentration of the latex.
6. Dilute solutions of alkalis, acids and of some salts give very good results.
7. If the quantity of the coagulant exceeds the minimum amount required for the coagulation of latex, no coagulation occurs and the latex passes into a second phase or zone.
8. When coagulation is effected by shaking, centrifuging, by the application of dry heat or by adding alcohol and acetone the p_H value of the latex remains unchanged.
9. Coagulation is also brought about by reagents used for hydration and dehydration and for precipitating proteins and also by micro-organisms and enzymes.

Our thanks are due to Mr. J. P. Anderson, Controller of Rubber, and Major H. R. Walden, Deputy Controller of Rubber and Officer-in-charge, Wild Rubber Section, Department of Supply, for the facilities and financial assistance for carrying out work on *Cryptostegia grandiflora* and other agricultural laticiferous plants in order to find out substitutes of *Hevea brasiliensis*.

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