

Chemistry : „*The coagulation of Hevea latex*”. By Dr. O. DE VRIES.
(Communicated by Prof. P. VAN ROMBURGH).

(Communicated at the meeting of January 27, 1923).

I. *Influence of the mixing-proportion of latex, water and acid,
irregular series.*

It was known from previous investigations, that the coagulation of Hevea latex with acids shows irregularities. The observations of several investigators, which we intend to discuss shortly in one of the following paragraphs (§ 9), had only been made occasionally, and did not give a sufficient insight into the phenomena; therefore it seemed desirable to us to obtain a total view of the proportions, by a systematical investigation into the complete range of mixing of latex—water—acid.

§ 1. *The Latex.*

Hevea latex is a milky liquid, which, under the microscope, appears to consist of oval globules, $\frac{1}{2}$ to 2μ in size, and showing a vivid Brownian movement; particles of less simple form occur now and then. The fact, that one has not to deal with globular particles, shows that latex is not a system liquid: liquid, an emulsion in the sense of Wo. OSTWALD's classification. On the other hand, one should not speak of liquid: solid (suspension); the properties of the coagulum obtained under various circumstances, make it probable that the rubber-particles in latex have a buttery consistency, i. e. between liquid and solid. If we have to look upon this as a more or less liquid nucleus, enclosed in a more solid superficial skin, as some investigators assume, is a matter we do not intend to discuss here. If we apply FREUNDLICH's classification of the colloids to latex, then undoubtedly it is a lyophilic colloid, as shown by the hydrous voluminous gel, obtained on coagulation, and by the behaviour of the latex with regard to dehydrating and salting-out substances; on the other hand, the hydrating power of the rubber-globules is decidedly only limited, and the latex, as regards its behaviour towards mono- bi- and trivalent anions, is strongly reminiscent of lyophobic colloids. So in this classification as well, latex

occupies an intermediate place. Moreover, the rather complicated properties of the latex may be understood, if we bear in mind, that it is a vegetable juice, in which besides the rubber-carbohydrates, also proteins, resins and other colloids play a part, and in which each in its turn may come to the front.

The composition of *Hevea* latex is not constant. The quantity of rubber and the quantity of secondary constituents depend on several factors, which cause changes in the physiological condition of the tree; moreover the tapping-system has a great influence. Besides we have to bear in mind, that after tapping the acidity of latex principally by bacteriological transformations, increases, even to such an extent, that after twelve hours "spontaneous" coagulation sets in.

If, however, circumstances are carefully chosen, it is an easy matter, to get a regular daily supply of latex of a certain composition. For that purpose one has to be restricted to a certain group of trees, from which, according to a certain tapping-system, latex is gathered daily, which moreover is always treated in the same way. The only remaining changeable factor, the meteorological circumstances, are then immaterial, if one keeps separate the latex of those days, on which in the morning the trunks were still wet, after nocturnal rains, or on which the latex gets drenched by an early shower.

We could, by taking these precautions very carefully, obtain quite sufficiently constant results, in the coagulation-experiments to be described here, with series of observations covering several weeks.

If, however, later on, one reverts to such observations with latex of a different group of trees, or a different tapping-system, the quantitative data do not correspond exactly any more, though the general course of the phenomena remains the same. In § 8 we intend to give a few examples of the differences caused thereby, and also of the influence of the gradually increasing acidity of the latex.

The results to be discussed here, have therefore to be interpreted in such a way, that the principal features of the view are generally available, but that the limits of the different ranges may be moved more or less, according to the composition of the latex with which one operates.

Against this drawback, that one operates with a non-constant, and not arbitrarily reproducible material, we find, as a great advantage, the fact, that *Hevea* latex is mixable with water in any proportion. So one may easily prepare all percentages of rubber from the original percentage (30—40 %) down to the lowest one, and one may, without great difficulty, traverse and search systematic-

ally in all directions the whole range of the mixing-proportions, by serial determinations with decreasing quantities of more or less diluted latex, and increasing quantities of acid; either diluted or not. The „irregular series” being only found with the lower percentages of rubber, it was possible to determine completely the range where these occur. In most cases, described in literature, the „irregular series” have only be examined with one single or with a few concentrations, the higher or lower concentrations of the colloid not being accessible. The latex, used for most of the observations to be described here, originated from a group of trees, fifteen years old, in the experiment garden at the opposite side of the Tjiliwoeng at Buitenzorg. The trees were tapped daily, with two cuts over $\frac{1}{4}$ of the circumference of the trunk, and the latex was used for examination between 10 a. m. and noon. The percentage of rubber (on coagulation) varied from 31,0 to 32,8, and on the average amounted to 31,8 %; the acidity was 0,02—0.04 N. (cf. § 8), the acids present are principally carbonic acid, lactic acid and a little butyric acid¹⁾.

In 1922 complementary observations were made with latex from a few groups of trees in the Botanical garden.

§ 2. *The phenomena of coagulation.*

With the proportions, as they are chosen in the practice of the preparation of rubber, the coagulation of *Hevea* latex proceeds slowly. After a quarter of an hour the liquid has become thick, with the consistency of porridge; gradually it begins to cohere, and after one hour a coherent lump is formed, but still with milky serum; only after a few hours the separation into a solid coagulum and a clear serum, is complete. In other cases one causes the coagulation to proceed more rapidly, by adding more acid, so that, after one hour, one obtains a coagulum sustable for working purposes. Or one saves acid, so that only after a few hours the first phenomena occur, and the coagulum can only be worked up next morning. Sometimes the latex is used undiluted, but mostly one dilutes with water to a rubber percentage of 20 or 15 %, on account of which the coagulum becomes softer, and may be worked up more easily. The more the latex is diluted, the softer the coagulum becomes, and the stronger the contraction after the coagula-

¹⁾ For the composition of *Hevea* latex in general we may refer to „Estate Rubber, its preparation, properties and testing” by Dr. O. DE VRIES (RUYGROK & Co., 1920), chapter 1 and 2.

tion will be, so that more serum is set free. Only with very strongly diluted latices a flocky coagulum is separated, which does not form a coherent lump, or only gradually coheres after one or more days. If we use less acid, the coagulation sets in slowly; but with decreasing quantity of acid the spontaneous coagulation, caused by bacteria which decompose the sugars and the proteins under formation of acid, begins to play a more and more important part. Ordinary, non-sterilised latex always coagulates, even without any addition of acid, during the first night after tapping; the coagulum is then spongy by the formation of gases, and the surface exposed to the air is covered with a yellow, evil smelling layer of porridge-like separated rubber, mixed with decomposition products of proteins. So in the range of very little acid there are no mixtures, which remain liquid in the long run; the observation "liquid" may be made after a quarter of an hour or after two hours, but after 24 hours one will find the mixture coagulated. The liquid mixtures with more acid, so in what one might call the second liquid range, remain liquid for an unlimited space of time. Sometimes, after being left to themselves for several days, a separation of very thin little flocks, lying on an almost clear or whitish serum, sets in, but in any case one can control and confirm the observation "liquid" after 24 hours. This liquid range passes into the ranges of coagulation by a strip of transition, being broad especially towards the side of the higher acid concentrations, and distinctly showing different stages. The first beginning of coagulation phenomena is the appearance of a thin skin at the surface of the liquid, caused by evaporation in the air, which, on stirring with a glass rod, attaches itself to it as a streak or rolls itself up.

On approaching the range of coagulation a little more, this streak becomes thicker and more cloddy. Advancing further, we get to clotting or curdling of a greater part of the latex; a pap and finally a coherent coagulum is formed. If it is left longer to itself, the coagulation in this range of transition proceeds further; what after two hours was a pap, may after 24 hours have become a coagulum and a mixture which after two hours only showed a thick streak, has changed the next morning into a pap, or even may be coagulated. What is liquid in the middle of the second range, remains liquid even after days, but "liquid" on the limit of "streaky", may have changed into streaky after 24 hours. "Coagulated" of course remains such after one or several days, only the coagulum gradually contracts itself a little and becomes harder.

It may be clear, that with these gradual transitions, we shall

never be able to fix any sharp limits for the different ranges. The ordinary discrimination, by gently shaking or stirring, can only be a rough one. We examined if sharper criteria might be found by means of the microscope, but it appeared, that the formation of little lumps of a few or a great many small rubber-globules also took place quite gradually, without sharp transitions, and that neither the decrease nor the stopping of Brownian movement opened the way for any sharp limitation.

So most of our serial experiments were confined to judging at sight, by means of a stirring rod, only completed occasionally by microscopic observations. A short time, about 15 minutes, after the addition of the acid the first observation was made, which in certain ranges is already sufficient. The principal observation followed two hours after the mixture was made, and was controlled the next morning, viz. if then a stage was reached so much further advanced as might be expected from the condition, such as it was two hours after the addition of the acid. In order to be able to sufficiently overlook the whole, we have, in the following paragraphs, interpreted the observations in a somewhat simplified way; therefore, with the classifications "streaks", "curdled", "porridge", and "coagulation" we have to associate the meaning of conditions of separation gradually passing into each other, as described above.

As a rule we worked with 50 cc. of liquid for each determination, the liquid being left open to the air in a small cylindric glass till the next morning, for the last control-observation. With very small quantities of acid the mixture of latex and water was measured with a measuring-cylinder and the acid was added by means of a burette. It was not necessary to measure the diluted latex more exactly than within $\frac{1}{2}$ or 1 c.c., but the acid had to be measured exactly within one drop, especially with the very diluted latices, where the range of coagulation is narrow and sharply limited. With mixtures with larger quantities of acid, the latex, either diluted or not, was always mixed with the diluted or undiluted acid in such quantities that the total volume was 50 c.c.; while the liquid, which occupied over half of the total volume, was poured out first, and the other one added to it.

Especially in the range of a large quantity of acid, or if one uses strong acid, it is necessary to stir vigorously from the beginning, so as to prevent local coagulation, which would cause enclosure of acid, not being set free any more by further stirring. By making one same final mixture, starting from latices of different dilutions

and differently strong acids, one may however control the observations in a satisfactory way.

On account of the increasing acidity of the latex itself it is not advisable to use it more than about two hours before the observations; we only did determinations between 10 a.m. and noon, but during that time one can easily prepare a few series, in total about thirty to fifty mixtures, so that in a rather short time by many hundreds of observations one can search the whole range of mixing in all directions.

Operating in small, open cylindrical glasses, causes a certain evaporation and results in the formation of a small superficial skin of coagulated rubber, which on stirring attaches itself to the stirring-rod.

Apparently this causes an undesired complication; but for distinguishing different liquid mixtures this formation of skin appeared on the other hand an advantage, because it enables us to recognize the liquids inclined to coagulate. By repeating a few series in small Erlenmeyer-flasks, closed with a cork, we have ascertained that really these skins are formed by evaporation at the surface.

§ 3. *Hydrochloric acid.*

The easiest way to summarise the phenomena at different dilutions and different quantities of acid, is to draw these in the wellknown triangle-figure. As angular points (components) we choose water, concentrated hydrochloric acid (9.14 N) and undiluted latex, i.e. a liquid with 31.8 % coagulable rubber, about 35 % totally solid substances and about 65 % water, and with an acidity of about 0.03 N. A recalculation of the results, so as to express these as quantity of acid, resp. rubber compared to the whole liquid (water of dilution plus serum) can never be correct by the phenomena of adsorption and, as regards rubber, there is not much sense in it, as coagulable rubber is a substance containing so many secondary substances in small quantities.

In the annexed figure 1 the lines show how the different mixtures are formed by mingling latex and hydrochloric acid, of different dilutions. The mixtures, in which after two hours a well coherent coagulum was formed, are marked with a little cross. As we see this range almost occupies the whole triangle; only in a narrow strip along the latex-water side, we find mixtures, which are represented by an encircled point (pap or curdling) or by a little circle (liquid), and there we can, though indistinctly on account of

the scale-size used, recognize irregular series liquid : coagulation : liquid : coagulation. This narrow strip, the range of small quantities

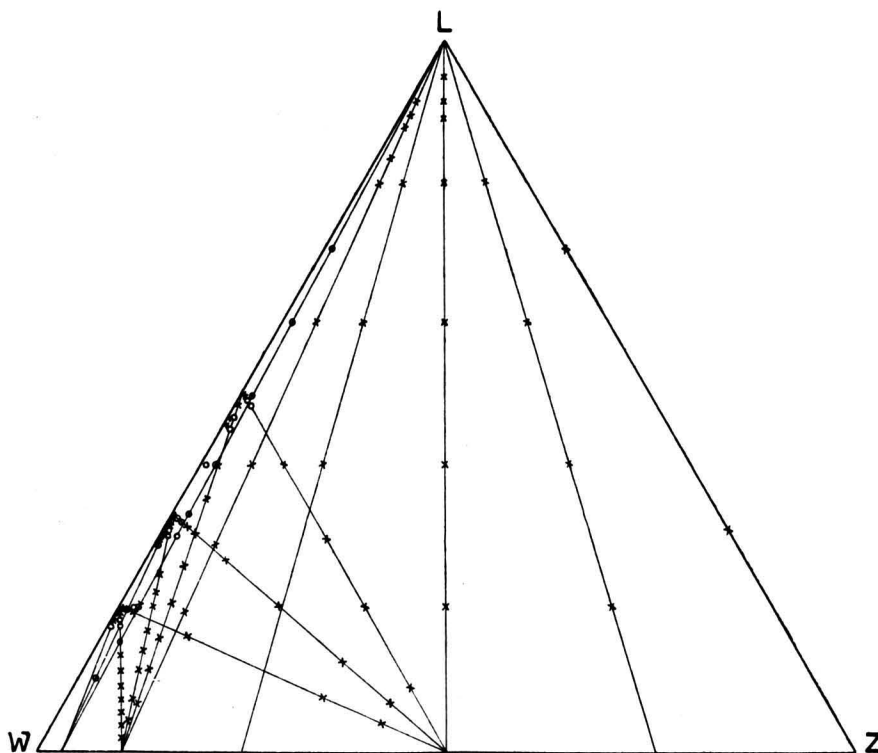


Fig. 1.

of acid, is, with hydrochloric acid, the only interesting item; the remainder of the triangle shows nothing particular, the less water the mixture contains, the harder the coagulum, while in mixtures with little water and much hydrochloric acid the serum assumes a violet tint.

The narrow strip along the latex-water side is represented on a larger scale in fig. 2, where the acid is drawn perpendicularly, as ordinate, and expressed in normality (grammolecules HCl per Liter final mixture).

For quite small concentrations of acid, at any dilution, we first come into the liquid strip, where coagulation has not yet started after two hours. After 24 hours this part shows spontaneous coagulation. At higher acid-concentration (from about 0.007 N) we find after two hours more or less strong curdling or formation of pap, and after 24 hours coagulation. The limit at which after two hours complete coagulation with a clear serum has taken place, is,

found with mixtures beyond 50% latex, to be fairly constant at 0.012 N. We should bear in mind, that this means the acidity of

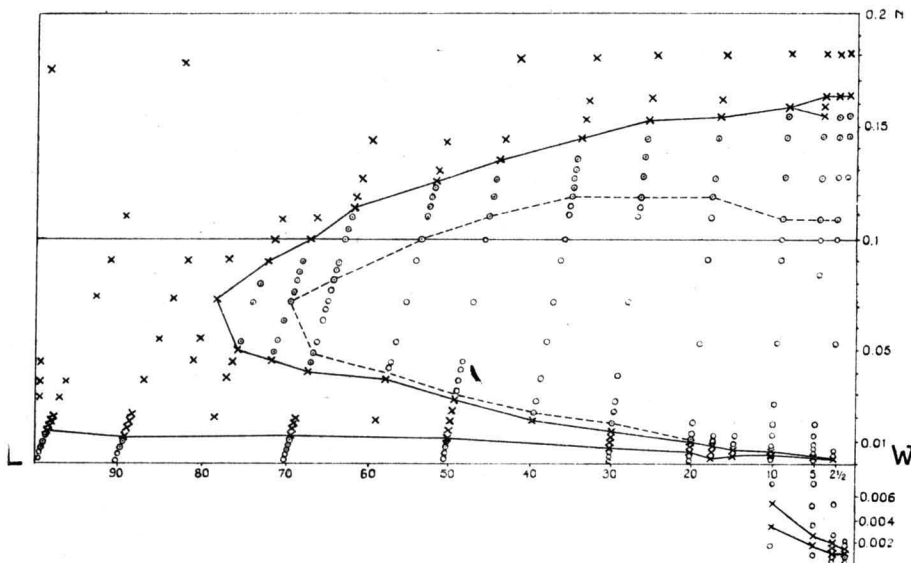


Fig. 2.

the hydrochloric acid added, which has to be increased with the original acidity of the latex, recalculated on the final mixture. For mixtures, containing less than 50% latex, this bottom-limit of coagulation is regularly lower. Because of reasons mentioned above, the observations could not be made so sharply that the relation between rubber-concentration and limit of acidity appeared quite clearly, but especially with the lower concentrations the small irregularities may be considered to be due to observation errors, and we may assume that the lowering of this limit is inversely proportional to the latex concentration.

With mixtures containing over 80% latex to which more acid is added we always get a strong coagulum, and so from the beginning we are in the range of coagulation, which fairly occupies the whole triangle of Fig. 1. At 75% latex we get the first indications that another phenomenon is about to appear, because the coagulum at first is hard, with more acid (about 0.05 N) soft or even like pap, and only with a still larger quantity of acid hard again. A distinctly liquid range only appears with mixtures with 65% latex and less.

The strip of coagulation between both liquid ranges, the lower range of coagulation, regularly decreases in latitude at lower latex-concentrations, but still remains distinctly perceptible even at the lowest concentrations (1% latex). In those very diluted liquids the

rubber does not separate itself as a coherent coagulum, but in the form of white flocks. The separation goes much quicker than with higher concentrations and with the liquids with 1 and $2\frac{1}{2}\%$ latex, reminds one of a titration of warm nitrate of silver with hydrochloric acid.

At those low concentrations the range of coagulation is so narrow, that, in an acidified but still unchanged liquid, one can see, with a single drop of diluted acid, the white flocks separating themselves, and that one sees the original milky liquid remain unchanged on addition of a few drops more. With mixtures with 5% latex one may get at first, with a small quantity of acid, a flocky separation, cohering fairly quickly as a coagulum; on addition of a little more acid a very soft coagulum may be formed at once. Mixtures with $2\frac{1}{2}\%$ and 1% latex cause flocky separations, which may remain unchanged for a long time, and with which the coherence as a coagulum is the more difficult, according as the mixture contains less latex.

At higher concentrations, just above 5%, sometimes the liquid separates itself in a remarkable quick way into a coagulum and a clear serum, but the instantaneous coagulation is not found there any more. At still higher concentrations the separation of the coagulum goes slower.

The lower range of coagulation, described here, is limited by a transition to spontaneous coagulation, as discussed above; at the upper part we find a narrow range of transition, where the mixture after two hours is like pap or curdling (after 24 hours mostly coagulated). Only towards the higher latex-concentrations this strip gradually becomes a little broader, and at about 65% latex bends itself in an upper direction, limiting the top of the liquid range, and converging into the broad strip, which separates the liquid range from the upper range of coagulation. Thus the liquid range is perfectly limited, both at the upper- and at the lower side, at least till the lowest concentration, which was examined (1% latex, so 0.3% rubber in the mixture). Whether, at still smaller concentrations, the lower strip of coagulation is continued, or if both the liquid ranges meet there, has not been examined yet. The limits of the various ranges are found at the following normalities of the added acid in the final mixture: (See Table following page).

These figures are illustrated by fig. 2.

We shall now give a short description of the course of the phenomena at a few typical concentrations. To the latex-water-mixture 10% hydrochloric acid (0.914 N) was added from a burette; the

TABLE I.

Latex in the mixture.	Lower limit of coagulation.	Upper limit first range of coagulation.	Upper limit liquid range.	Lower limit second range of coagulation.
65 %	0.012	0.04	0.08	0.10
50 %	0.011	0.029	0.10	0.13
40 %	0.009	0.019	0.11	0.14
30 %	0.007	0.013	0.12	0.15
20 %	0.005	0.009	0.12	0.155
10 %	0.0035	0.0055	0.11	0.16
5 %	0.0018	0.0027	0.11	0.155
2½ %	0.0009	0.0018	0.11	0.16
1 %	0.0008	0.0011	0.14 ?	0.16

quantities were chosen in such a way that the final mixture was always 50 cc., so that the latex-concentration, at larger quantities of hydrochloric acid, decreased a little, and that the serial determinations in fig. 2 are found on slanting lines.

With a mixture with 70% latex the result of the examination two hours after the addition of acid was (cf. fig. 2):

After being left to itself for three hours, the coagulation of course had proceeded further; now 2½%, had become a pap, 2¾% a thick liquid with a good many skins, 3—4¾% remained liquid, 5¾% was softly coagulated. The mixtures in the strips of transition show a further advanced coagulation, but the true liquid mixtures remain liquid, even after 24 hours. When it is left in open small cylindric glasses, a skin is formed at the surface, evidently by evaporation, for in closed Erlenmeijer-flasks it was not formed. So the limits of the ranges are somewhat displaced, according to the moment of observation being delayed, but the phenomenon coagulated — liquid — coagulated remains. It strikes us, that the transition at the lower side of the liquid range is very acute; at the upper side however much more gradual. The little skins formed on stirring, are partly due to evaporation at the surface, or to latex, drying upon the side of the glass; yet these skins point to a higher inclination for coagulation, as such mixtures after 3 or 24 hours are coagulated further than the purely liquid ones.

c c. 10 % HCl per 50 c c mixture.	DESCRIPTION.
0.1	liquid.
0.3	liquid.
0.4	thick pap; beginning of strip of transition.
0.5	thick liquid, a few little lumps.
0.6	the same.
0.7	a somewhat thick pap, coagulating on stirring; beginning of the range of coagulation.
0.8 and 0.9	strong coagulum, serum white.
1	coagulated, serum fairly clear, (acid added 0.018 N).
2	the same, serum fairly clear.
2 $\frac{1}{4}$	the same, serum white. Upper-limit first range of coagulation.
2 $\frac{1}{2}$	liquid, a few small lumps on stirring. Therefore sharp transition.
2 $\frac{3}{4}$	liquid with some skin.
3	liquid; lower limit liquid range.
3 $\frac{1}{2}$, 3 $\frac{3}{4}$, 4, 4 $\frac{1}{4}$	liquid; no skin.
4 $\frac{1}{2}$	liquid, on stirring some skin or streak. Upper-limit liquid range.
4 $\frac{3}{4}$	the same, a piece of skin (therefore irregularity).
5, 5 $\frac{1}{4}$	the same, more skin.
5 $\frac{1}{2}$	the same, a fair quantity of skin.
5 $\frac{3}{4}$	like pap (at an other time only a fair quantity of streaks).
6	very soft pap, almost coagulated.
6 $\frac{1}{4}$	coagulated, but serum quite white, therefore far from complete. Lower-limit second range of coagulation.
6 $\frac{1}{2}$	coagulated, fairly stiff, serum white.
7	the same, serum white.
8	the same, serum white. The percentage of latex in this mixture is 58.8 %.

An other example with 30 % latex: (See following page).

Of course the coagulum is always soft, because the mixtures only contain 30 % latex, i.e. about 10 % rubber.

Quite typical are the sharp transitions at the first range of coa-

c c 10 % HCl per 50 c c mixture.	DESCRIPTION.
0.1	liquid.
0.2	liquid.
0.3	liquid, somewhat thickish, small lump of coagulum.
0.4	coagulated, rather stiff, serum rather clear, lower limit first range of coagulation.
0.5	coagulated, serum clear.
0.6	coagulated, serum perfectly clear like water.
0.7	well-formed, but soft, jellied coagulum, serum nearly clear. Upper limit first range of coagulation.
1	quite liquid, only somewhat streaky, lower limit liquid range. Sharp transition.
1 1/4, 1 1/2, 2, 4	quite liquid.
6	quite liquid, somewhat streaky, like 1. (later determination liquid without streak).
6 1/4	liquid.
6 1/2	liquid, somewhat streaky, upper limit liquid range.
7	liquid, rather streaky.
8	for the greater part liquid, a good deal of streaky soft coagulum.
8 1/2	soft coagulum, serum white. Lower limit second range of coagulation.
9	soft coagulum, serum white.
10	well-formed but soft coagulum, serum quite white.
11	the same the same.
12	the same serum almost clear.

gulation of very dilute latices; e.g. at 1 % latex (0.3 % rubber in the mixture), see fig. 2, lower, enlarged part.

The microscopic image of the liquid in the second liquid range, is, e.g. for a mixture with 2 % latex, as follows.

At a small acid-concentration almost all the rubber-globulus are still free from each other, and have a Brownian movement; only very few small lumps are seen, consisting of some little globules touching each other. Starting from an acid-concentration of about 0.02 N to increase somewhat, but by far the greater part of the particles are still free and in vivid Brownian movement. Only at

cc 1 % HCl	DESCRIPTION
0.25	liquid, containing a few small flocks.
0.4	liquid, with a few small flocks.
0.45	after about $\frac{1}{4}$ hour rising flocks are separative, so that after 1 hour the serum is almost clear.
0.	coagulates almost momentarily in flocks, rising to the surface in a layer, serum almost clear.
0.55	flocks are separated slowly. serum remains white.
0.6	liquid.
1.0	liquid.

about 0.11 N, i.e. at the upper-limit of the liquid range (see fig. 2), the number of small lumps increases and the Brownian movement decreases, and at 0.13 N hardly any particles move, and only very few show Brownian movement. At 0.14 N the decreaming begins, which, at 0.15 N, leads into the range of coagulation. From 0.10 to 0.15 N therefore, there is a gradual transition from "free particles with Brownian movement" into lumps, particles yet free but not moving, and decreaming. Whether perhaps the few little lumps, which are found in the second liquid range, were formed by a local excess of acid during addition, was not examined.

If we keep a liquid from the middle part of the second liquid range, e.g. 2 % latex with 0.06 N. hydrochloric acid, in a high cylindric glass, no decreaming takes place within the first few weeks, but the Brownian movement gradually decreases. After two months most of the particles have joined into small lumps, a few consisting of two or three, but most of them consisting of a great number of globules, so that, after that time, only a fairly small number of free particles remain in Brownian movement; yet only part of the rubber is decreamed, and superficially the liquid is still equally white.

We regret we were unable to examine, whether in the second liquid range the negative charge, which the rubber-globules show in the original latex, had given place to a positive one, as required by the theory of „change of charge” ¹⁾. Some experiments concerning

¹⁾ Cf. F. POWIS, Z. Phys. Chem. 89 (1915), 105.

H. R. KRUYT, these Proceedings 17 (1914), 615, and 19 (1917), 1021.

the coagulation with different salts, will be described in a following communication.

We shall discuss in § 8 a few examples of the influence of the original acidity of the latex on the position of the limits of the ranges.

§ 4. *Nitric acid.*

We likewise made serial determinations with nitric acid and sulphuric acid, but less detailed, so that the limits of the different ranges were only roughly determined. For these experiments latex was used from a different group of trees, containing 28 % rubber. Fig. 3 gives the determinations for nitric acid. The general type is

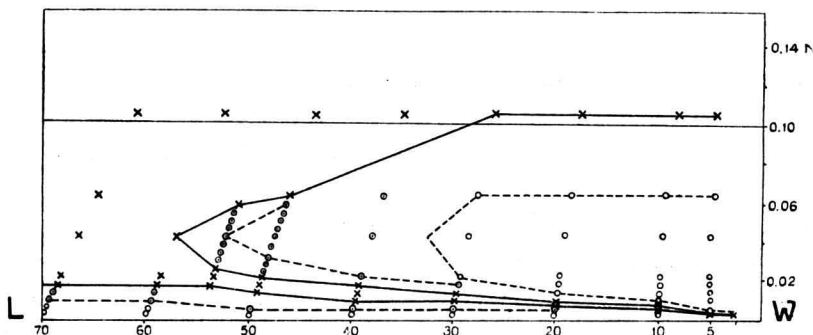


Fig. 3.

exactly the same as with hydrochloric acid, both the liquid and the pappy ranges are smaller. Fig. 3 only goes as far as mixtures with 70 % latex; the top of the pappy range, being with hydrochloric acid at 75 % latex and about 0.07 N, is found here at a little less than 60 % latex and about 0.04 N. The top of the totally liquid range is comparatively still more displaced towards the right, so that, between both these tops, a very wide „pappy” range is found, in which we separated, by a dotted line, that part where, after two hours a thick or fairly thick pap is formed, from the part still showing fairly liquid mixtures with streaks or a beginning curdling. With nitric acid the upper-limits lie at about half the normality of that with hydrochloric acid.

In § 7 we intend to compare more closely the figures for the four acids, and also discuss more detailed the data for mixtures with 5 and 2 % latex.

§ 5. *Sulphuric acid.*

The data, which we gathered for coagulation with sulphuric

acid, have been put together in fig. 4. The large range of coagulation at acid-concentrations above 0.1 N (normal = 49 Gr. H_2SO_4 per Liter) has again been quite left out, and also the mixtures with over 70 % latex, where coagulation constantly takes place as soon as more than 0.01 N acid is added. On account of the smaller number of observations, the course of the limits in fig. 4 seems to be somewhat irregular, yet the data are sufficient to

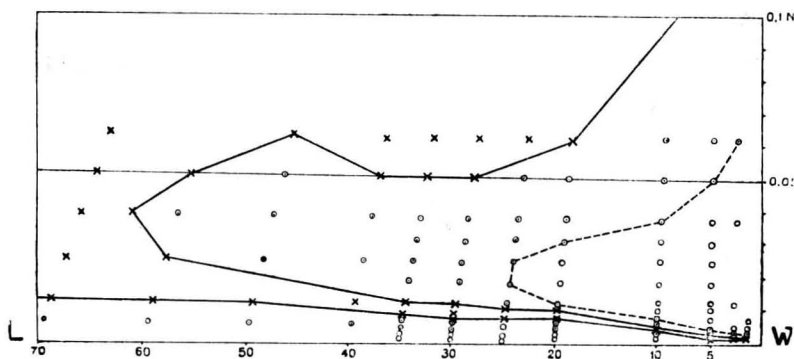


Fig. 4.

conclude, that the pappy and the liquid range, compared with hydrochloric acid and nitric acid, have shrunk still more. Figures of comparison are again found in § 7.

We may still mention, that, starting from a mixture with 70 % latex, we get a distinct indication regarding the existence of the „irregular series”, though all the mixtures coagulate; the mixture with 0.04 N. acid gives a perceptibly softer coagulum than that with 0.025 or 0.05 N. acid.

§ 6. *Acetic acid.*

For acetic acid — the general and usual means of coagulation at rubber plantations — the course of the phenomena generally speaking appears to be the same as in the previous cases, but the proportions of the various ranges are quite different ones. Whilst with the three previous acids the whole range of the irregular series lies in a narrow strip along the latex-water side, which in a representation like fig. 1 is hardly discernible, the irregular series with acetic acid are extended to far higher acid concentrations, and a triangle-figure like fig. 5 opens the best general aspect. Here likewise the range of coagulation occupies by far the greater part; viz. almost $\frac{3}{4}$ of the triangle; but in the neighbourhood of the

angularpoint for water we find that over $\frac{1}{4}$ of the triangle is occupied by the liquid and pappy range, while naturally in this case also, close along the latex-water-side a first liquid range is found, not showing any coagulation on addition of a very small quantity of acid, but, after keeping, showing spontaneous coagulation by the action of bacteria.

The proper liquid range in fig. 5 is again limited by a dotted line; the pappy range is divided by a somewhat thicker dotted line into two parts, a fairly liquid and a more pappy one. Formation of a coherent coagulum takes place in the narrow strip parallel to

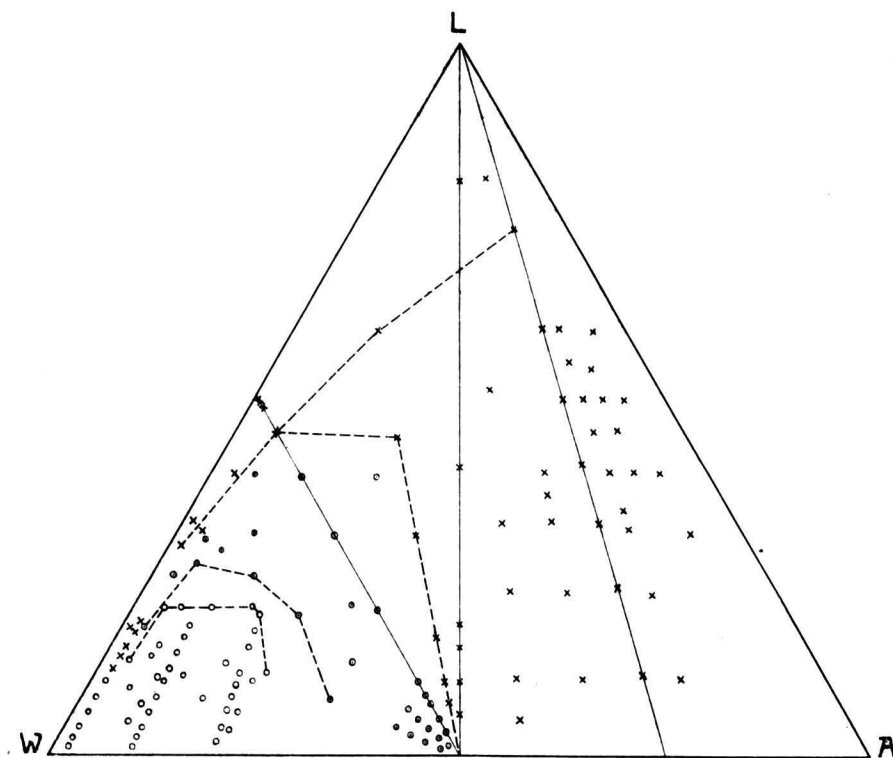


Fig. 5.

the latex — water — side and towards the side of the angular-point Latex; the total range towards the side of the angular-point acetic acid gives a perfect coagulation, but in the shape of flocks or as a pap, and not as a coherent lump. Both these ranges of coagulation are roughly separated in fig. 5 by a dotted line. Therefore in this respect too, there is an important difference between acetic acid and the three other acids, with which the whole range of coagulation gives a coherent coagulum.

We traced the coagulation with acetic acid once more by a considerable number of determinations, viz. in the latex of both the above-mentioned groups of trees; in fig. 5 we have represented the results, obtained with the 28 % latex of the second group (see § 4). The normality of acetic acid added is given in table 2 for the limits of the various ranges.

TABLE 2.

	Quantity of latex in the mixture in %.									
	100	80	60	50	40	30	20	10	5	2½
Limit lower liquid range.	0.004	0.003	0.003	0.003	0.003	—	0.003	0.0015	—	—
Beginning lower creamy range.	0.008	0.008	0.008	0.009	0.009	—	0.009	0.003	—	—
Lower limit range of coagulation.	0.017	0.024	0.031	0.030	0.028	—	0.016	0.006	0.0015	0.0012
Upper limit first range of coagulation.	—	—	—	0.52	0.35	0.21	0.13	0.08	0.05	0.026
Lower limit second liquid range.	—	—	—	—	—	—	0.8	0.24	0.16	0.10

On comparing these figures and fig. 5 with the results described in §§ 3—5, we distinctly see the great difference in the distance between the limits. A comparative review is given in § 7.

In judging the above figures one has to bear in mind, that the phenomena, in the sense in which we consider them here, are not exactly the same as in plantation practice. So here we take as lower limit of the range of coagulation those mixtures, where a coherent coagulum is formed after two hours, whilst with regard to the coagulation at the plantations it is moreover required, that the serum is clear or almost clear, and the coagulum sufficiently stiff to be mangled. With undiluted latex the lower limit of the range of coagulation, as it is described here (0.017 N or about 1 Gram acetic acid per Liter latex), will be lower than the amount used in practice, if we wish to mangle a few hours after the coagulation. With 50 % latex (i. e. 1:1 diluted) the dose (0.030 N = 1.8 Gr. acetic acid per Liter) is higher, because with diluted latex one

mangles the next day, when with a much smaller quantity of acetic acid, a coagulum fit for use has formed itself.

To this we add the results of a less complete series of observations, made in November 1922 with latex from the Botanical garden at Buitenzorg, where a few groups of trees were tapped with a cut over $\frac{1}{4}$ of the circumference.

This latex contained 37 % rubber, and had an acidity of about 0.025 N. We see that the general type is the same, that the lower limits fairly well coincide, but that, with regard to other limits, rather important differences appear, that may be attributed partly to the difference in composition and acidity of the latex, partly however, to the difference of appreciation between the observers. This example illustrates, together with the cases to be discussed in § 8, the restriction we made already in § 1, regarding the quantitative value of the results.

TABLE 3.

	Quantity of latex in the mixture in %.							
	80	60	40	20	10	5	2	1
Beginning lower creamy or pappy range.	0.009	0.010	0.009	0.006	0.0026	—	—	—
Lower limit first range of coagulation.	0.018	0.022	0.017	0.009	0.0053	0.0026	0.0020	0.0016
Upper limit first range of coagulation.	—	—	0.40	0.20	0.083	0.04	0.033	0.023
Lower limit second liquid range.	—	—	—	0.5	0.17	0.066	0.059	0.040

§ 7. *Comparison of the four acids.*

We now intend to compare amongst each other the results, obtained with the four acids. Whilst, roughly speaking the general course is exactly the same, we may notify interesting differences and conformities.

Considering first of all the top and the upper limit of the liquid range, we can use for that purpose the data mentioned in § 3—6, although they refer to two different latices, and the principal observations covered a period of over half a year, because these limits, can only be roughly determined. So we get:

TABLE 4.

	HCl	HNO ₃	H ₂ SO ₄	C ₂ H ₄ O ₂
Top liquid range, with mixtures with latex	70 _{0/0}	35 _{0/0}	25 _{0/0}	25 _{0/0}
Top pappy range, with mixtures with latex	77 _{0/0}	57 _{0/0}	65 _{0/0}	57 _{0/0}
Upper limit liquid range for 20 % latex, at acidity	0.12 N	0.06 N	0.03 N	3—4 N
Upper limit pappy range (lower limit second range of coagulation) for 20 % latex, at acidity	0.155 N	0.10 N	0.06 N	7—8 N

The limit, at which irregular series do not appear any more — the top of the pappy range — is found for nitric acid, sulphuric acid and acetic acid at almost the same percentage of latex, but for hydrochloric acid it is somewhat higher. With all this we have to bear in mind that with nitric acid in a mixture with 60 %, with sulphuric acid in one with 70 %, a distinct interruption in the series can still be observed, owing to the coagulum, at a level of the above-mentioned top, being softer than at higher or lower concentrations of acid. A striking difference in the position of this top cannot therefore be stated with the four acids.

On the other hand there is an undeniable difference with regard to the top of the really liquid range, which, with hydrochloric acid extends to much higher latex-concentrations, than with the three remaining acids.

In the upper limit of the liquid range, i.e. the beginning of the upper curdling range, and likewise in the upper limit of this range, i.e. the lower limit of the second range of coagulation, the difference is very striking too. With acetic acid these limits are by far the highest; then follows hydrochloric acid, about halfway lower nitric acid, and half way lower again sulphuric acid. If we assume, that in the second liquid range the colloid rubber particles have changed their charge from negative into positive, the stronger coagulating action of the bivalent sulphate-ion would be fully explained; mono-valent ions then would show a decided difference in the series nitrate-, chlorine-, acetate-ion.

A comparison of the action of the four acids in the first range of coagulation seemed of particular interest to us, viz. with small latex-concentrations, where, with a small increase of the acid-

concentration we so sharply get with the three inorganic acids the phenomenon liquid-rapid coagulation-liquid, described in § 3. Therefore, for the same mixture of latex, we once more determined these limits for all four acids separately, in order to get absolutely comparable figures (which figures therefore do not fully correspond with those in §§ 3—6, as we explained in § 1 and intend to discuss more in detail still in § 8).

The figures were for the acid-concentration in normality:

TABLE 5.

	HCl	HNO ₃	H ₂ SO ₄	C ₂ H ₄ O ₂
5 % latex, lower limit	0.0011	0.0011	0.0011	0.0015
5 % latex, upper limit	0.00265	0.00265	0.0029	—
2 % latex, lower limit	0.0007	0.0007	0.0007	0.0010
2 % latex, upper limit	0.0013	0.0013	0.0014	—

The lower limit of the range of coagulation is exactly the same with the three strong inorganic acids, and here it is quite clearly demonstrated, that, at least in this range of strongly diluted latices, the phenomenon is ruled by the positive H-ions; the action of acetic acid is somewhat weaker.

With hydrochloric acid and nitric acid the upper limit again is exactly the same; also the strips of transition (which are very narrow with these strongly diluted latices) show exactly the same phenomena if the same quantity of acid is added; so the action of hydrochloric acid and nitric acid in the lower range of coagulation is exactly the same, whilst the limit of the upper range of coagulation, as we have seen just now, is considerably lower with nitric acid. With sulphuric acid the upper limit of the first range of coagulation is a little higher; the difference is not important, but for all that, with this exclusively comparative experiment, it could be stated clearly, also because corresponding differences were noticed in the strip of transition lying above the range of coagulation. With acetic acid the upper limit is much higher (at about 0.05 and 0.026 N, see table 2) and has not been determined again in this experiment.

A determination of the hydrogen-ions concentration in these various liquids, which would be necessary for a correct interpretation of the phenomena, could not as yet take place; we only wish to draw the attention to the fact, that the subsequency of the four acids at

the upper limit of the first range of coagulation (hydrochloric acid and nitric acid — sulphuric acid — acetic acid) is not the same as at the lower limit of the second range of coagulation (sulphuric acid — nitric acid — hydrochloric acid — acetic acid).

§ 8. *Influence of the acidity of the latex itself.*

As already stated in § 1 latex is feebly acid, and on being left to itself gradually increases in acidity. The acidity of the latex, which is used for the researches, is of course not without influence on the figures obtained, though the relation need not be purely additive, as the acidity in latex is caused by carbonic acid and organic acids amongst which, after the action of bacteria, lactic acid, acetic acid and butyric acid.

First of all we made a few observations in ordinary latex and in the same latex after neutralisation with hydroxide of potassium, i.e. again for the limits, to be fixed sharply, of the first range of coagulation in mixtures with little latex. A mixture with 5% latex (percentage of rubber 1.43% needed) for the neutralisation (phenolphthalein as indicator) 16.6 cc. $\frac{1}{10}$ N hydroxide of potassium per Liter, and therefore was 0.00166 normal; for the original latex we calculate from these data an acidity of 0.033 N. A mixture with 2% latex (percentage of rubber 0.54% required) 6.6 cc. hydroxide of potassium and therefore was 0.00066 normal (i.e. also 0.033 N calculated for original latex).

The limits of the first range of coagulation appeared to be with hydrochloric acid:

TABLE 6.

	Own acidity	Addition hydrochloric acid in normality	
		Lower limit	Upper limit
5 % latex, original	0.00166	0.0015	0.0032
id. , neutralized	—	0.0030	0.0048
2 % latex, original	0.0066	0.0013	0.0020
id. , neutralized	—	0.00195	0.0027

We see, that the neutralization has increased the necessary addition of acid with about the amount of the own acidity of the latex. In judging the figures we should bear in mind that the neutralized

latex contains by the neutralization a small quantity of potassium salts, that may somewhat displace the limit of the ranges.

A second experiment related to the increase of the own acidity of the latex, when left to itself. The latex used for this purpose titrated, when left to itself undiluted, at 10 o'clock 0.026, at noon 0.030 and at 1.45 p.m. 0.032 N. From the observations resulted:

44½ cc. 70% latex, diluted at 10 o'clock with 5½ cc. 10% HCl (i.e. mixture 0.1 normal, belonging in the upper pappy range of transition, see Fig. 2): after one hour still liquid, but containing a fair-sized lump of streaks, and after three hours a thick pap, fairly well coagulated, with quite white serum;

the same mixture, but prepared only at 12.30 p.m. from the undiluted latex, was already coagulated, after being left to itself for one hour, though the coagulum was still very soft. So the influence of the higher own acidity of this latex was quite noticeable.

43 cc. 40% latex, prepared at 10 o'clock with 7 cc. 10% HCl (i.e. about 0.13 N, again in the middle of the upper pappy range of transition, see Fig. 2) caused after one hour a small lump of little skins, and was still liquid after three hours with a fairly strong skin;

the same mixture, prepared at 12.30 was still liquid after one hour with a small lump of skins, which was somewhat larger than in the above-mentioned mixture after one hour. So in this case the difference was noticeable, though not important.

It appears from these experiments, as might be expected, that,

TABLE 7.

	May 1920	Oct 8th 1920	Oct. 9th and 12th 1920	Oct. 14th 1920	May 1922
Own acidity undiluted latex	0.026— 0.030	—	0.041— 0.044	0.033	0.022
Upper limit 5 % latex	0.0027	0.0025	0.00265	0.0032	0.0044
Lower limit ib.	0.0018	0.0012	0.0011	0.0015	0.0020
Upper limit 2½ % latex	0.0018	—	—	—	—
Lower limit ib.	0.0009	—	—	—	—
Upper limit 2 % latex	—	0.0014	0.0013	0.0020	0.0026
Lower limit ib.	—	0.0007	0.0007	0.0013	0.0014
Upper limit 1 % latex	0.0011	—	—	—	0.0020
Lower limit ib.	0.0008	—	—	—	0.0014

by operating with the latex later, the quantity of acid that has to be added in order to reach a certain stage, is found to be a little smaller.

We will still give a few examples, how much the percentages of acid found may vary when latex from different origin is used, viz. for hydrochloric acid and for the limits of the first range of coagulation with mixtures with 5 and 2% latex.

If we calculate the differences in own acidity of the diluted latices, we see that the differences in acidity for the limits differ fairly strongly from them, though a general relation can be clearly noticed. In fact a strictly quantitative correspondence could not be expected as the latices differed not only in acidity but also in percentage of rubber and in secondary substances.

§ 9. *Investigations of others.*

As mentioned in the introduction, we find in literature a good many investigations, pointing to the existence of irregular series with Hevea latex.

J. PARKIN, one of the first investigators who was engaged with acid-coagulation of Hevea latex¹⁾, used for his experiments ten times diluted latex and stated therewith the transition liquid — coagulated — liquid. PARKIN, whose experiments were limited to small additions of acid, did not notice the second range of coagulation. As an explanation PARKIN assumed, that the protein, present in latex, is insoluble in a neutral liquid, but dissolves in alkali or acids. PARKIN was of opinion that Hevea latex is alkaline; therefore addition of acid would first cause neutralization, with precipitation of the protein and, as a result, of the rubber as well, whilst, at a higher acidity the protein would dissolve again. PARKIN further stated that with acetic acid the range of coagulation is wider than with other acids, and thought this a decided advantage for practice, because by addition of too much acid the coagulation would not fail so soon.

Because in the practice of plantations one never causes the percentage of rubber of the latex to sink below 15 or 12 % (i. e. in our terminology, one never uses mixtures with less than 50 to 40 % latex), where with acetic acid no irregular series occur, there was for a long time no further interest for these phenomena. W. CROSSLEY²⁾ again gave a few figures for upper — and lower limit of the

¹⁾ Circulars Royal Botanic Gardens Peradeniya Vol. I (1899), 149.

²⁾ India Rubber Journal 41 (1911), 1206.

first range of coagulation with a mixture with 7 % rubber (i. e. about 25 % latex) which had been preserved with formaline. We found the lower limit at 0.014 N. acetic acid, the upper limit at 0.29 N, whilst the own acidity of the diluted latex was 0.015 N. These figures correspond fairly well with ours (tables 2 and 3). CROSSLEY's lower-limit is somewhat lower and his upper-limit somewhat higher, whereby the unknown action of formaline, may have been of influence. Moreover CROSSLEY determined the lower limit of the first range of coagulation for dilutions of the above-mentioned latex with 7 % rubber, and found that, as far as a hundredfold dilution, the total acidity (acetic acid added plus calculated own acidity) decreased with great exactness proportional to the percentage of latex. For dialysed latex with a percentage of 12 % totally solid substance (i.e. a mixture with about 40 % latex) CROSSLEY¹⁾ found the following figures for the lower- and upper-limit of the first range of coagulation:

TABLE 8.

	Lower limit	Upper limit
Acetic acid	0.02 N	0.18 N
Trichloroacetic acid	0.005	0.026
Formic acid	0.008	0.022
Hydrochloric acid	0.004	0.016
Sulfuric acid	0.005	0.018

The dialysed latex had an acidity of only 0.001 N; all the limits (except the upper-limit with sulphuric acid) are lower than those we found for normal latex, so that the dialysable serum substances in natural latex would have an anti-coagulating action.

As a criticism of these investigations B. J. EATON²⁾ published a few series of observations with hydrochloric acid, nitric acid, sulphuric acid and acetic acid, which however are very incomplete and did not throw much light on the phenomena; EATON found mixtures which remained liquid, but this he attributes to a retardation of the coagulation on account of high dilution, or to an inclusion of the acid in the little lumps on partial coagulation. EATON denies the

India Rubber Journal 42 (1911), 1345.

Bull. of the Dept. of Agric., Fed. Malay States No. 17 (1912), p. 10.

existence of a maximum-limit for the first range of coagulation, as fixed by CROSSLEY; from the above it is perfectly clear that this criticism is absolutely without ground, and that the maximum-limit, described by PARKIN and CROSSLEY does really exist; but only with mixtures with a percentage of latex below a certain limit.

G. S. WHITBY¹⁾ was the first one who emphatically pointed out the existence of the second range of coagulation above the second liquid range and described a few complete series liquid coagulated — liquid — coagulated. WHITBY for these phenomena assumed the explanation that small quantities of acid have an activating influence on an enzym, which is found in latex, coagulase, which, at a small acidity, would cause the coagulation, but at a higher acidity would become inactive; the second range of coagulation then would be a direct precipitation of protein by larger quantities of acid.

We shall now compare the observations of the last two investigators with our own.

1. *Hydrochloric acid.* In Fig. 6 the limits have been taken from Fig. 2, and therein have been drawn the observations made by EATON and WHITBY.

Starting from undiluted latex EATON found with 10% acid (line 1 in fig. 6) a continual series of coagulations, but with 1% acid

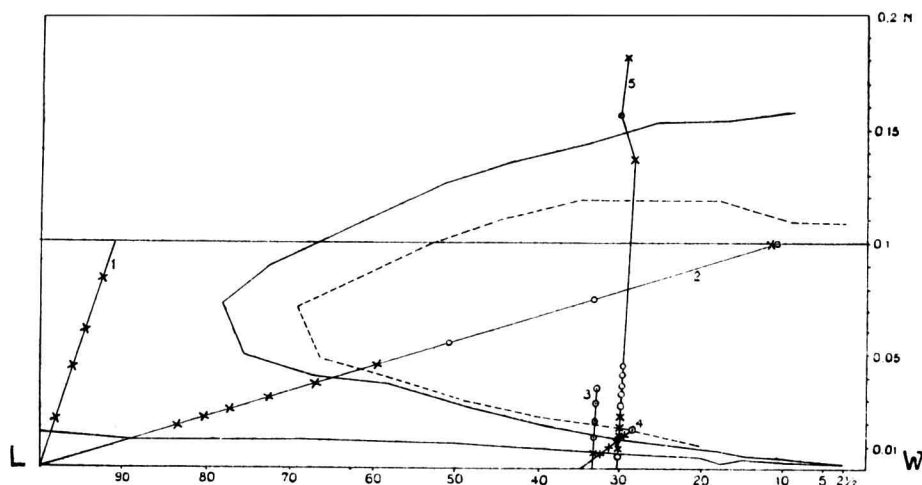


Fig. 6.

(line 2) he got into the liquid range. Two series with 1 : 2 diluted

¹⁾ Zeitschr. Koll. Chem. 12 (1913), 156, India Rubber Journal (London) 45 (1913), 945; further Agric. Bull. of the Dept. of Agr. F.M. S. (Kuala Lumpur) 6 (1918), 381.

latex (our $33\frac{1}{8}\%$) showed him the transition from coagulated to pappy, but did not show distinctly, that he had got again into the second liquid range (lines 3 and 4). EATON did not observe the upper range of coagulation.

WHITBY made a complete series at about 30% latex; his limits do not fully coincide with ours, which for the reasons already mentioned (own acidity latex etc.) is not astonishing, and also may be caused by wrong reproduction, as WHITBY does not mention the exact titre of his hydrochloric acid. So except small differences the observations of both investigators fit satisfactorily in the frame of our recapitulating-figure (see fig. 6 and 2).

2. *Nitric acid.* EATON made two series of observations, starting from undiluted latex, and always found coagulation at increasing acidity, corresponding with Fig. 3. Moreover a series with 1% acid with 1:2 diluted latex, with which he passed from the range of coagulation into a pappy range ("incomplete coagulation"), which again he attributes to the above mentioned causes (inclusion of acid in the lumps).

WHITBY also described for nitric acid a complete series, viz. for a latex with 12% rubber (corresponding with a mixture with 40% latex); he found at 0.016 N coagulation, at 0.021 a pap, at 0.032 and 0.052 liquid mixtures, at 0.063 a pap again, at 0.105 and 0.21 coagulation. These observations tally with ours (see Fig. 3), except both the liquid mixtures (WHITBY only says "coagulation failed to occur", which possibly may correspond with our mixtures with a little curdling).

3. *Sulphuric acid.* EATON made a series with undiluted latex, which (as might be expected) showed coagulation at all acidities; moreover one with latex diluted 1:3 where after the range of coagulation came a few mixtures with incomplete coagulation, and a series with latex diluted 1:10, where coagulated—incompletely coagulated—liquid was stated. The fact of remaining liquid is attributed again by EATON to a retardation of the coagulation with strongly diluted latex, but he does not explain in which way he accounts for the coagulated mixtures with less acid found in this series.

WHITBY only gives a short indication about a series liquid—coagulated—incompletely coagulated (pap)—coagulated, without mentioning the percentages of acid and the percentage of rubber. Probably this has been the same diluted latex with 10% rubber (30% latex) as in his experiments with hydrochloric acid, and therefore WHITBY probably remained at a concentration, up to which the liquid range does not reach. (cf. Fig. 4).

4. *Acetic acid*. EATON again mentions a few series with undiluted and diluted latices, in which for the diluted latices the pappy, skinny or liquid range was reached at acidities, corresponding fairly well with those found by us. For this acid WHITBY does not give any quantitative data, but only says that the first range of coagulation is much wider than with the previous acids, and that, after that, liquid mixtures are reached. With 30 % latex we did not find any liquid mixtures (top at 25 % latex), but probably WHITBY's mixture had come, by the addition of diluted acetic acid, to a lower percentage of rubber. WHITBY did not find an upper limit of the liquid range, as could not be the case (see Fig. 5) on dilution of 30 % latex with acetic acid of less than 50 %.

As we see, the data of both these investigations fit in a satisfactory way in the frame of our recapitulating-figures and their observations, partly seeming confused, are explained by the system of ranges, as they have become known to us at present.

SUMMARY.

Mixtures of Hevea Latex and water show, on addition of acids, the phenomenon of the irregular series. For hydrochloric acid, nitric acid, sulphuric acid and acetic acid the limits of the ranges (first and second liquid range, first and second range of coagulation, strips of transition) were completely fixed for all mixing-proportions of latex, water and acid (see fig. 1—5), and a comparison was made between the position of the limits for these four acids.

Buitenzorg, December 1922.
