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Rheology of Fresh Latex from Hevea Collected over Successive Intervals from Tapping

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Early- and late-flow fractions of Hevea **brasiliensis** *latex were exposed to repeated shear. The late-flow fractions showed a response which could only rarely be evoked in the early-flow fractions. The response is known to be attributable to lutoids in the latex, and it is inferred that lutoids in the late-flow fractions were in a superior or more active condition than those in the early-flow fractions.*

A simple microviscometer with which thixotropy due to lutoids in fresh latex was demonstrated was described in a previous paper (SOUTHORN, 1968). The method showed that the latex samples required were small, permitting examination of latex fractions taken at intervals during the latex flow after tapping. There are already indications that differences exist between such latex fractions in the extent of lutoid damage (PAKIANATHAN *et al.*, 1966). If there are differences in the surface condition of the lutoids, these would be expected to induce changes in rheology, particularly with regard to thixotropy. An investigation of the rheological properties of early and late fractions of fresh latex during flow was therefore undertaken, using a modified form of the Southorn microviscometer.

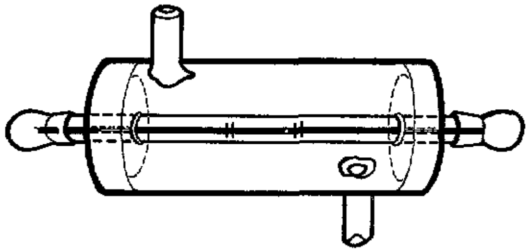

Figure 1. Modified Southorn microviscometer.

METHODS AND RESULTS

In the rolling ball microviscometer as originally described (SOUTHORN, 1968) no provision was made for temperature control. The instrument was modified by the addition of a jacket coaxial with the capillary through which water at a controlled temperature was circulated *(Figure 1)*. The capillary was engraved with marks 1 cm apart and used at an angle of 25° from the horizontal, the method being to measure the roll-time of the stainless steel ball between the marks with a tilt angle of 25° in one direction and then back again to the original mark with the capillary tilted at 25° in the opposite direction. The time taken for the ball to make the 1 cm journey in both directions (returning to the original mark) is referred to as the 'roll-time.' Since a short period is required to brake and accelerate again at the end of each journey, starting and stopping marks were also engraved 1 mm beyond the timing marks on the capillary; the practice was to tilt the capillary from horizontal with the ball on the starting mark, time it along the 1cm course and allow the ball to overshoot to the stopping mark when the tilt was reversed and the ball returned. The instrument was calibrated with glycerol/water mixtures of known viscosities at 25°C, and gave a linear response as shown in *Figure 2*.

In a preliminary series of experiments the behaviour of a sample of fresh whole latex was examined, the ball being rolled for ten

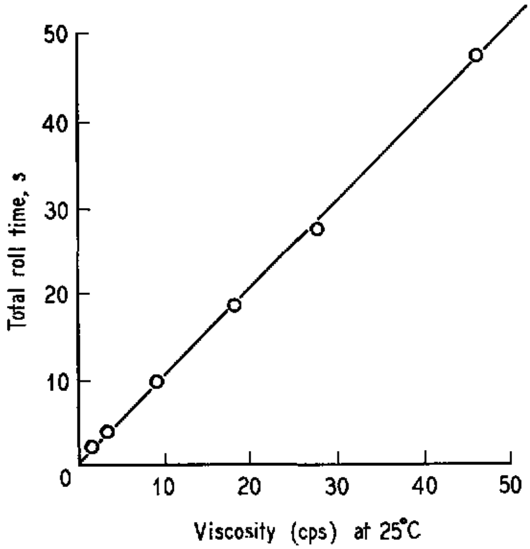

Figure 2. Calibration of microviscometer using glycerol/water mixtures at 25°C.

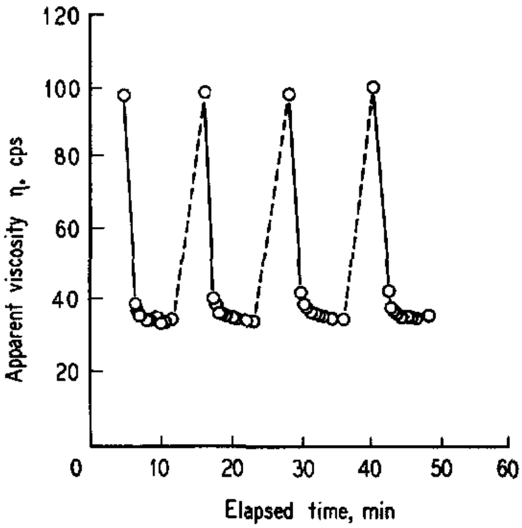

Figure 3. Thixotropic behaviour of fresh latex.

complete journeys without rest and then allowed to rest for 5 minutes. Plots of apparent viscosity against elapsed time at 25°C gave a similar pattern to that reported earlier by SOUTHORN (1968), who showed that the rise in apparent viscosity on resting was due to reversible structure building (*i.e.* thixotropy) between the lutoids contained in the latex. *Figure 3* shows the results obtained.

To put these results in a convenient form, the rise in apparent viscosity over a fixed time period of rest was taken as a measure of the rate of structure formation. *Figure 4* is an idealised representation of a typical observation. The difference between the apparent viscosity indicated by the first reading after the rest period (η^r) and the base level apparent viscosity (η^t) was recorded as $\triangle\eta$. Changes in the value of η^t are related to irreversible changes in the general colloid stability of all the particles in the latex, including the rubber; as the latex becomes unstable η^t rises. Changes in the value of η^r are related to the thixotropic behaviour of the lutoid component only (SOUTHORN, 1968), and $\triangle\eta$ is a measure of the extent of mutual

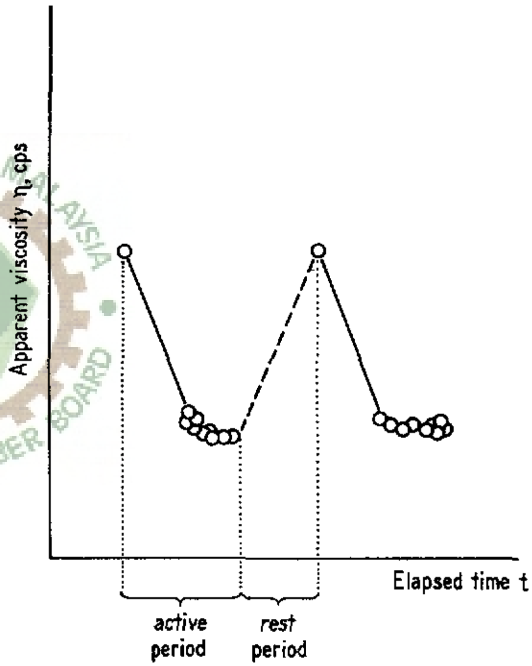

Figure 4. Idealised representation of relationship between apparent viscosity and shear (for details see text).

adhesion which occurs between lutoids during the rest periods, the structures so formed being broken down during the active periods of the experiment.

Figure 5 shows the effect of resting time at 25°C on $\Delta\eta$ for two collections of fresh whole latex. The rate of increase in $\Delta\eta$ is reasonably linear for up to 10 min rest; thereafter the rate diminishes, probably because after 10 min most of the lutoids available for structure building are already participating effectively. A standard rest period of 5 min was therefore adopted as a basis for comparison. One or two experiments of long duration had to be interrupted, giving a single rest period of more than 5 min at some point. In such cases the results of the first 'active period' after resumption of the experiment were disregarded.

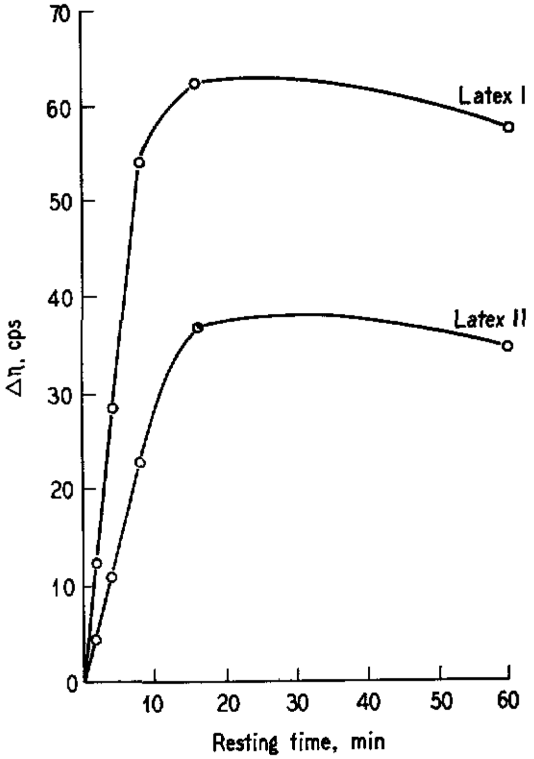

Figure 5. Effect of resting time on $\Delta\eta$ at 25°C for two latices.

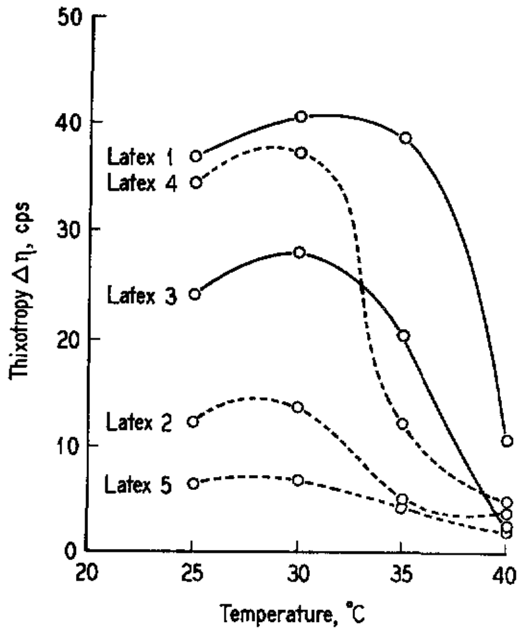

Figure 6. Effect of temperature on $\Delta\eta$ for five latices.

In the next series of experiments the effects of temperature on $\Delta\eta$ for 5-min rest periods were explored. Five collections of fresh whole field latex from a range of clones were examined at temperatures from 25° to 40°C *(Figure 6)*. The curve obtained shows a slight rise in $\Delta\eta$ for increasing temperature up to about 30°C, followed by a considerable lowering of $\Delta\eta$ at higher temperatures. The most likely explanation is that lutoids become increasingly unstable as temperature increases. At first this instability shows as an increased tendency towards aggregation, but at still higher temperatures the lutoids begin to break down completely and there is a reduction in the number of whole lutoids available for the type of structure building observed in these experiments. In the light of these results a standard temperature of 25°C was adopted for all further experiments, as being a readily-maintained and relatively safe temperature as far as lutoid breakdown is concerned.

General Characteristics of Different Flow Fractions

For studies of latex flow fractions, latex was collected in the field under chilled conditions at various intervals after tapping. The early or first-flow fraction was collected for 5 – 10 min immediately after tapping; the second-flow fraction was collected 15 min after tapping for 15 min and the late or third-flow fraction was collected 30 min after tapping for 15 minutes. The fractions were quickly brought back to the laboratory and filtered first through muslin and then through stainless mesh of 28η aperture to remove any large aggregates already present. The filtered fraction was placed in the microviscometer at 25°C. The ball was rolled for ten to-and-fro journeys between the two marks 1 cm apart before being allowed to rest for 5 min with the viscometer in a horizontal position. After the initial rest period the ten to-and-fro passages of the ball were repeated and the roll-time for the total distance of 2 cm in both directions of tilt was recorded for each journey. The viscometer was again returned to the horizontal position for another 5 min before further readings were recorded. These procedures were carried out with all the three fractions.

Two collections of fresh latex were investigated and the thixotropic build-up of the different flow fractions is shown in *Figure 7*. There was very little thixotropy in the first or early-flow fraction, comparatively much more in the second-flow fraction and even more in the third or late-flow fraction, indicating the presence of more sensitive and active lutoids in the later-flow fractions. The marked differences in behaviour between the early- and late-flow fractions might be due to a progressive change with time. To investigate this possibility the more extreme (early and late) fractions were again studied, this time continuing the viscometry for a much longer period.

Early- and late-flow fractions were collected as described earlier. The steel ball in the microviscometer was rolled for five complete journeys before it was allowed to rest for 5 min and measurements carried out as before. The behaviour of each fraction in the microviscometer was followed for a maximum of 4 hours. The results are shown in *Figure 8* (early-flow fractions) and *Figure 9* (late-flow fractions). The early-flow fractions generally showed no particular pattern, the results being somewhat scattered, suggesting incipient instability of the rubber particles. However, in one experiment *(Figure 8e)* there was a steady rise in $\Delta\eta$ over a period of 3h, followed by a fall. The late-flow fractions showed similar effect but to a more marked degree.

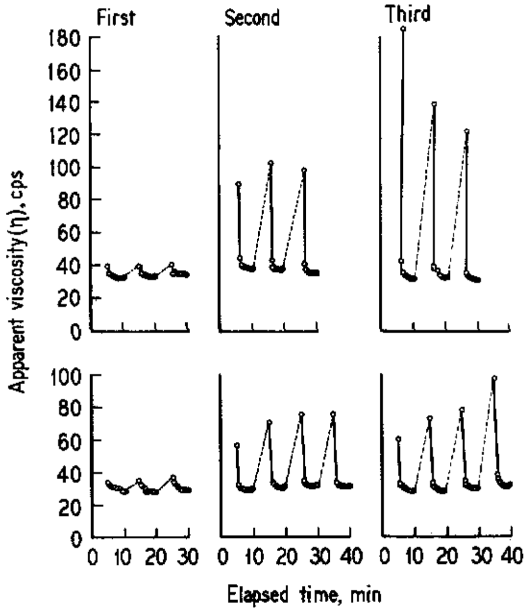

Figure 7. Thixotropic behaviour exhibited by different latex flow fractions collected at three time intervals after tapping. Data from two experiments.

Further experiments were carried out with early- and late-flow fractions obtained from the same latex collection. Measurements of both fractions were taken at the same time, and *Figure 10* shows two of the eight latex collections investigated. The peak value of $\Delta\eta$ ($\Delta\eta$ max.) measured in experiments on twenty-one latex collections ranged from 2½ to 42 cp for early-flow fractions

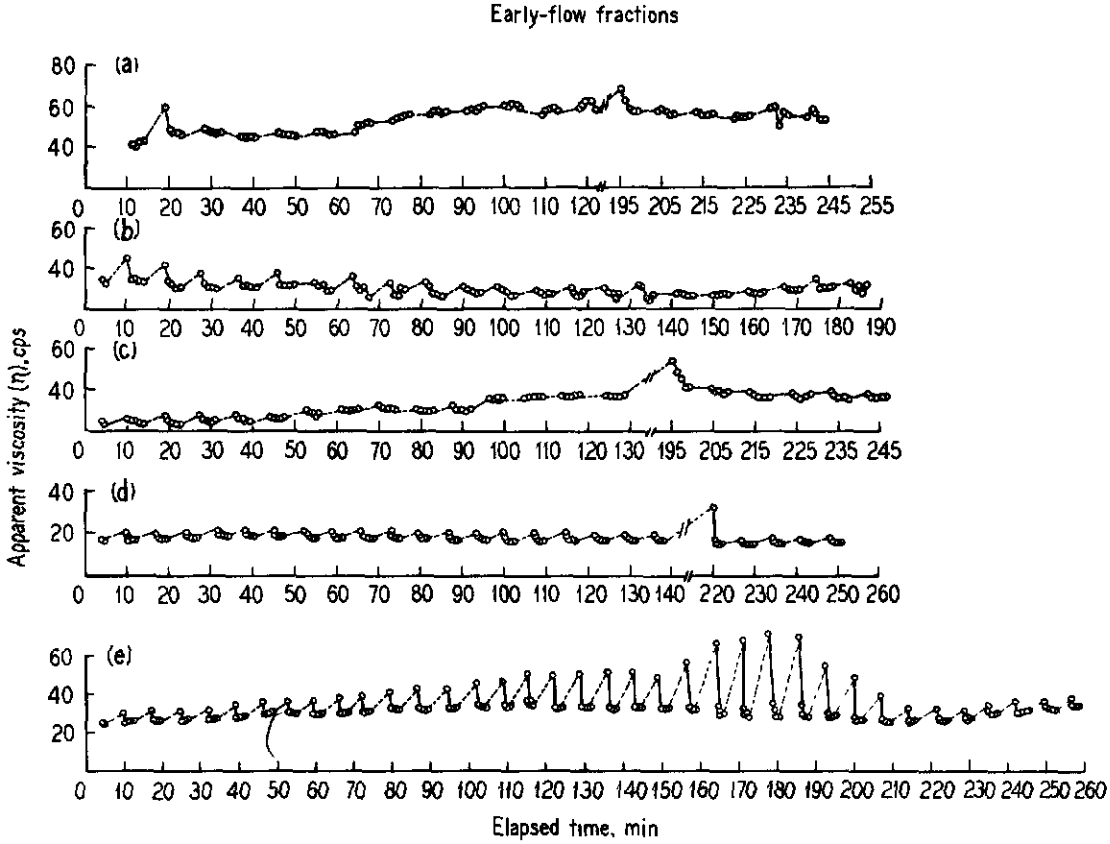

Figure 8. Behaviour of five early-flow latex fractions in microviscometer over a period of 3 – 4 hours.

and from 17 to more than 300 cp for the late-flow fractions. The early-flow fractions thus showed a much lower activity than the late-flow fractions.

These experiments suggest that under the conditions of repeated shear, latex can respond in a way which results in an increase in $\triangle\eta$ (as measured by this technique) to a temporary high value; this effect is seen only to a minor degree in the early-flow fractions, whereas it is readily reproducible and very pronounced in the late-flow fractions. These remarks apply to latices tested for prolonged periods under the repeated shear conditions of the measurement, and it was therefore of interest to investigate the kind of changes that would take place with time if latex is left undisturbed.

Portions of early- and late-flow fractions collected as before were each tested soon after being brought to the laboratory, and other portions were reserved for testing some hours later. The results are shown in *Figure 11*. The early-flow fractions (a_1) showed very little change in $\triangle\eta$ in the initial test, and no response in the test after 3½ h rest (a_2). The late-flow fraction, from the same latex collection, showed very strong $\triangle\eta$ peaks, both in the initial test and in the test after 3½ h rest, with the interesting difference that the rested portion developed its $\triangle\eta$ peak more speedily — suggesting that changes in

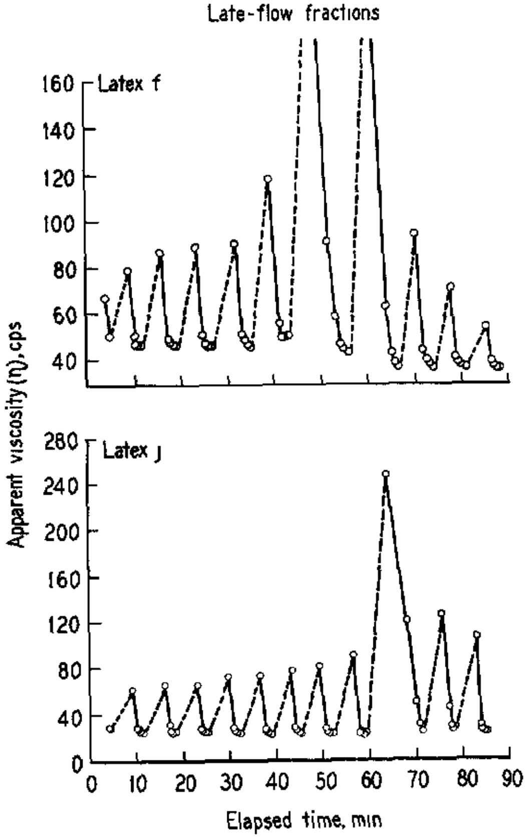

Figure 9. Thixotropic behaviour of latex flow fractions in microviscometer over 1½ hours.

thixotropy which can occur under experimental conditions of shear can also occur, though more slowly, on storage.

Effect of Dilution

The experiments hitherto described demonstrate an effect in the late-flow fractions which was rarely seen in the early-flow fractions. There are theoretical reasons (discussed later) why intact lutoids in a good polarised condition might be expected to exhibit the behaviour shown, and there are experimental and theoretical grounds for expecting that damaged lutoids are likely to be found in the early-flow fractions. The

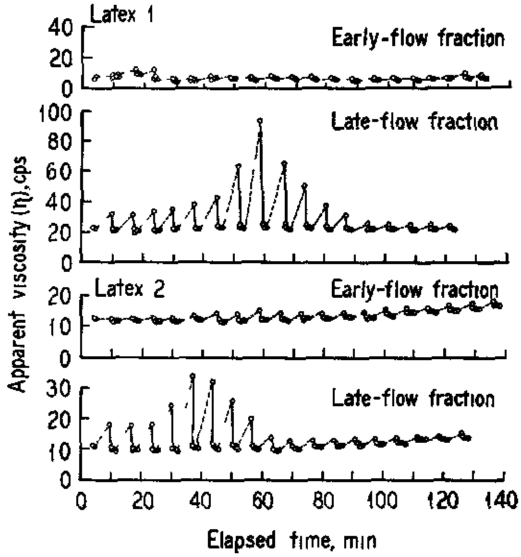

Figure 10. Thixotropic behaviour shown by the early (first) and late (third) latex-flow fractions from the same collection.

observed behaviour was therefore thought to be a consequence of the superior condition of the lutoids in the later-flow fractions.

An alternative explanation which would have led to a different conclusion was also considered. It is known that the addition of small amounts of water to field latex brings about a sharp rise in bulk viscosity, which is usually attributed to swelling and mutual adhesion of bottom fraction particles. It is also known that in the course of latex flow, water is injected into the latex by the 'dilution reaction' of the tree. If the late-flow fractions are regularly more dilute than the early-flow fractions, it could be argued that the positive effects observed indicated osmotically damaged lutoids rather than that the lutoids were more intact.

Two sorts of experiments were carried out to test this hypothesis. Firstly, the percentage of total solids in early- and late-flow fractions were compared to see whether there was any indication that the late-flow fractions were regularly more dilute. No such consistent dilution was observed *(Table 1)*. In the

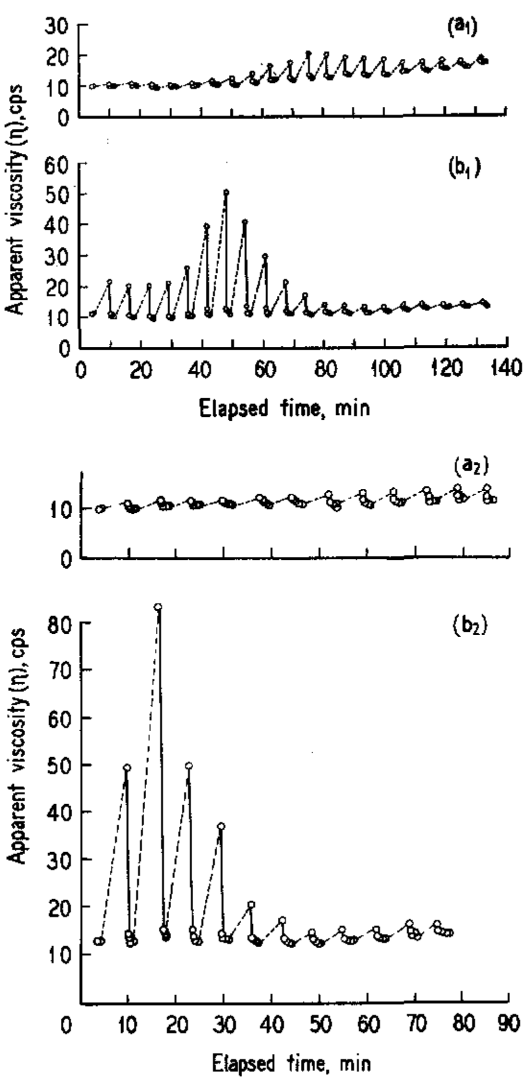

Figure 11. Thixotropic behaviour of the early (a_1) and late (b_1) flow fractions from the same latex collection during the initial test, as compared with that of the early (a_2) and late (b_2) flow fractions from the same latex after 3½ hours.

TABLE 1. TOTAL SOLIDS (%) IN EARLY AND LATE LATEX FLOW FRACTIONS

Latex	Total solids (%)	
	Early-flow fraction	Late-flow fraction
1	43.5	41.4
2	37.8	34.9
3	31.3	36.6
4	35.5	36.8
5	40.6	43.5
6	39.3	41.2
7	40.6	40.1

second series of experiments early- and-late flow fractions were both examined for thixotropy with and without addition of water to see whether dilution could cause a similar increase in thixotropy. In no case was it possible to provoke the observed effect by adding water to the latex.

DISCUSSION

It is unfortunate that experiments cannot be conducted on lutoids as they exist in the latex vessel. In the course of tapping, processes are initiated which subject lutoids to a variety of disruptive agencies, particularly during the first few minutes of latex flow. It is not surprising that the lutoids of the early-flow fractions ('early' lutoids) show more signs of gross damage than those collected from the late-flow fractions ('late' lutoids), as was first demonstrated by PAKIANATHAN *et al.* (1966). 'Late' lutoids are likely to approximate more closely to lutoids in the vessels than are 'early' lutoids.

There are good reasons for supposing that the lutoid membrane is very complex (GOMEZ AND SOUTHORN, 1969) and that in the latex vessel it is electrically polarised (SOUTHORN AND ESAH YIP, 1968). It may also be electrically excitable (LIM *et al.*, 1969). Whether excitable or not, such a polarised membrane will undergo a series of changes in physical properties as it loses its original highly organised structure (SOUTHORN, 1969).

The sequence of changes to be expected is:

1. Loss of polarisation
2. Increase in permeability
3. Disintegration

In the first stages of depolarisation, there will be a partial neutralisation of the negative electrical potential on the exterior surface of the membrane (as the potentials of the interior and exterior surfaces equilibrate). During this phase there will be a tendency for lutoid particles to adhere and aggregate so as to maintain charge density by reducing the net surface area exposed to the ambient medium (C-serum).

The present results can be explained on the grounds that the late-flow fractions usually still contain a proportion of lutoids with intact polarised membranes. When exposed to repeated shear stress in the viscometer these lutoid membranes are depolarised, and it is possible to follow the changes in mutual adhesion between them which accompany this process. The depolarisation still takes place but after a longer time, if the latex is stored. When latex is stored for a period before testing in the viscometer, the longer the storage the less is the period required under shear in the viscometer before signs of depolarisation appear — the effects of storage and shear are additive. Once depolarisation has occurred, no amount of subsequent storage or other treatment will repolarise the membranes. This is probably the reason why the effect could occasionally not be detected in a particular latex collection — depolarisation had occurred before the test.

The latex from early-flow fractions rarely shows the effect at all, or if it does so, then only weakly. It is concluded that latex from early-flow fractions contains few lutoids capable of this response to shear.

All these results are consistent with the hypothesis that lutoids are subjected to a lower intensity of stress in the later stages of flow. The late stages of flow are now shown to contain lutoids still capable of physical reactions such as have been postulated to occur within the latex vessels. It is evident that in any further studies on such reactions it would be advisable to start with material which is still relatively intact, and the lutoids from the late-flow fractions would be the material of choice.

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