

Streaming Potential Measurements on Solid Rubber Surfaces

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An experimental study of electrical potentials generated by streaming an electrolyte solution through rubber capillaries is reported. The measurements were used to derive zeta potentials. The influence of electrolyte pH, capillary former, rubber composition and capillary rinsing with electrolyte were examined. Data acquired suggest a role for the experimental technique in the characterisation of solid rubber surfaces.

Understanding of the stability of rubber latex remains incomplete despite decades of effort¹⁻³. The mechanism at play when rubber meets a solid surface in the presence of water, such as skidding road tyres, is still not fully understood⁴⁻⁶. Both phenomena have in common the electrical charging of the rubber surface. An estimate of this for a solid rubber surface can be obtained by streaming electrolyte solution over the surface to yield the *zeta* potential. The aim of the investigation described here is to measure the variation of *zeta* potential with electrolyte pH for a range of rubber materials selected to reveal different aspects of the surface charges present. Such charges may have a bearing upon both the stability of latex and the boundary lubrication of solid rubber.

For natural rubber latex, micro-electrophoresis^{7,8} and moving boundary electrophoresis^{9,10} have been used to investigate the electric charge on latex particles, but it is difficult to calculate the *zeta* potential from measurements of electrophoretic mobility because of the wide distribution of particle size in the latex. Furthermore, little correlation has been found between the electrophoretic mobility and mechanical stability of latex¹⁰. Streaming potential measurements on solid rubber yield *zeta* potentials without the need for any knowledge of particle size.

It is believed¹¹ that the electrical charges on natural rubber particles in latex derive from a surface layer of proteins and higher fatty acids. The spontaneous rise in mechanical stability when fresh ammoniated latex concentrate is stored has been shown to correlate with the increase in surface layer soaps arising from the hydrolysis of some lipids.

Many of the solid rubber samples used for the streaming potential measurements in this investigation were prepared from latex by dipping. It may therefore be expected that similar charged species will be present on the solid rubber samples as were present on the original latex particles used to make the solid rubber.

Streaming potential measurements on rubber have been carried out previously using synthetic rubber capillaries formed by hot compression moulding of the glass tubes into solid blocks of rubber and then removing the glass after vulcanisation¹². This produced 100 mm long rubber capillaries of 1.5 - 1.8 mm bore. Difficulties were experienced at each stage of their manufacture due to the ease with which the glass tubes broke. When a similar procedure was tried using glass rods, the same difficulties were experienced. To overcome such problems, latex dipping was employed. In this way the

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rubber capillaries could be readily and accurately made on glass and stainless steel formers.

This type of work could lead to better characterisation of solid rubber surfaces, which could help the industry to decide on such matters as the adhesion, friction and wear of rubber articles. The results reported are for both natural and synthetic rubber capillaries. *Zeta* potential values are compared as a variation with pH for the range of materials studied.

THEORY

When an electrolyte solution is forced through a capillary tube under an applied pressure P a streaming potential E develops between the ends and for laminar flow, this can be related to the *zeta* potential ζ at the solid-liquid interface by the formula:

$$\frac{E}{P} = \frac{\epsilon \zeta}{4\pi\eta k} \quad \dots 1$$

where ϵ and η are the dielectric constant and viscosity of the solvent, respectively, and k is the specific conductance of the electrolyte solution in the capillary.

If C is the cell constant and R the capillary resistance then Equation 1 may be rewritten as:

$$\zeta = \frac{4\pi\eta}{\epsilon} \cdot \frac{E}{P} \cdot \frac{C}{R} \quad \dots 2$$

$$\text{where } k = \frac{C}{R}$$

At 20°C using aqueous solvents, with η in poise, R in ohms and P in centimetres of mercury, this becomes:

$$\zeta (mV) = 1.059 \times 10^5 \cdot \frac{E}{P} \cdot \frac{C}{R} \quad \dots 3$$

EXPERIMENTAL

The practical aspects of this investigation consisted of constructing the necessary glass-ware, preparing the sample rubber capillaries, arranging electrical equipment, making up electrolyte solutions and carrying out the various streaming potential tests.

Glass Apparatus

A diagram of the apparatus is shown in Figure 1. This was constructed by suitably bringing together the necessary component parts made of borosilicate glass. The cell electrodes were silver/silver chloride prepared by electrolysis of clean, 0.5 mm diameter silver wire in 0.1M KCl at 2mA for 8 h, using platinum wire as cathode. The gas pressure needle valve (Edwards, type LV5) was used for applying variable pressure to the electrolyte via a 5-litre flask as gas ballast. The gas used was compressed nitrogen free of carbon dioxide and its applied pressure (5–25 cm Hg) was measured with a mercury manometer. Taps, sleeves and seals were made of PTFE to avoid using grease in the joints.

Rubber Capillaries

Capillaries of natural rubber were prepared by dipping borosilicate glass formers (1.5 – 1.8 mm diameter) into the rubber latex [low-ammonia (LA), high-ammonia (HA) or deproteinised (DP)]. The former was held in an electrically controlled dipping machine (Cotswold 7R.4.3.30) to give slow advance and withdrawal of the former into the latex.

The usual procedure was to lay down four thin coats of the latex, leach in distilled water for 1 h at 60°C–70°C, followed by two more straight dips of the same latex and then four coagulant dips [40% $\text{Ca}(\text{NO}_3)_2$ in ethanol, 5 min dwell] of prevulcanised latex (Revultex HR) to build up the capillary wall thickness for adequate strength. The capillary on its former was leached in distilled water before drying at 70°C. For comparison, a 'deproteinised' rubber capillary was also made from some fifty thin coats built up by straight dipping into DP latex.

The dried rubber-coated glass formers were soaked in warm distilled water (60°C–70°C) and allowed to leach for 16 h. After soaking, it was generally found that with care, a glass former could be loosened and withdrawn to leave a rubber capillary with a glass-smooth internal surface (Figure 2). Such capillaries after drying at 70°C, were cut to length and used directly in the apparatus used for streaming

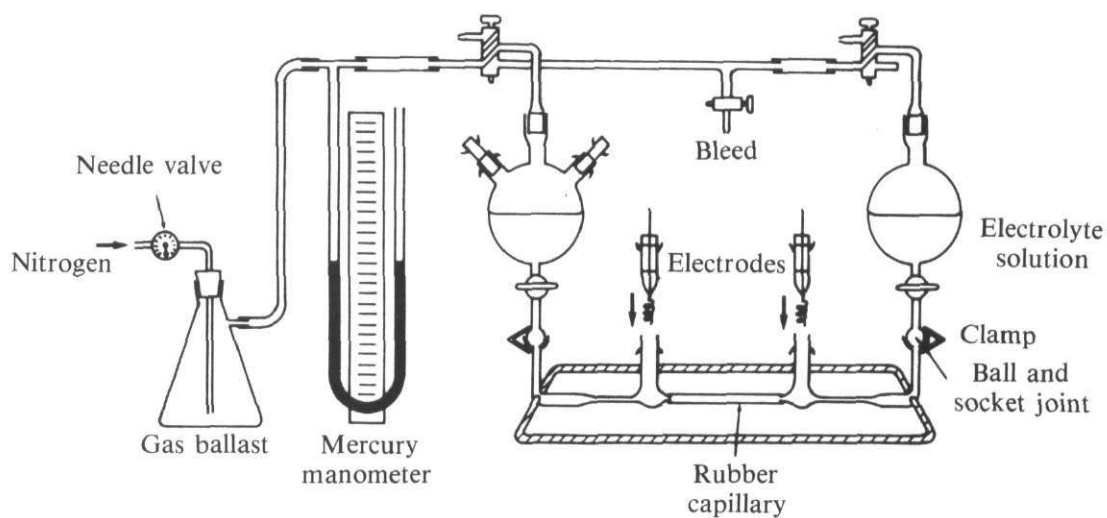


Figure 1. Apparatus for streaming potential measurements.

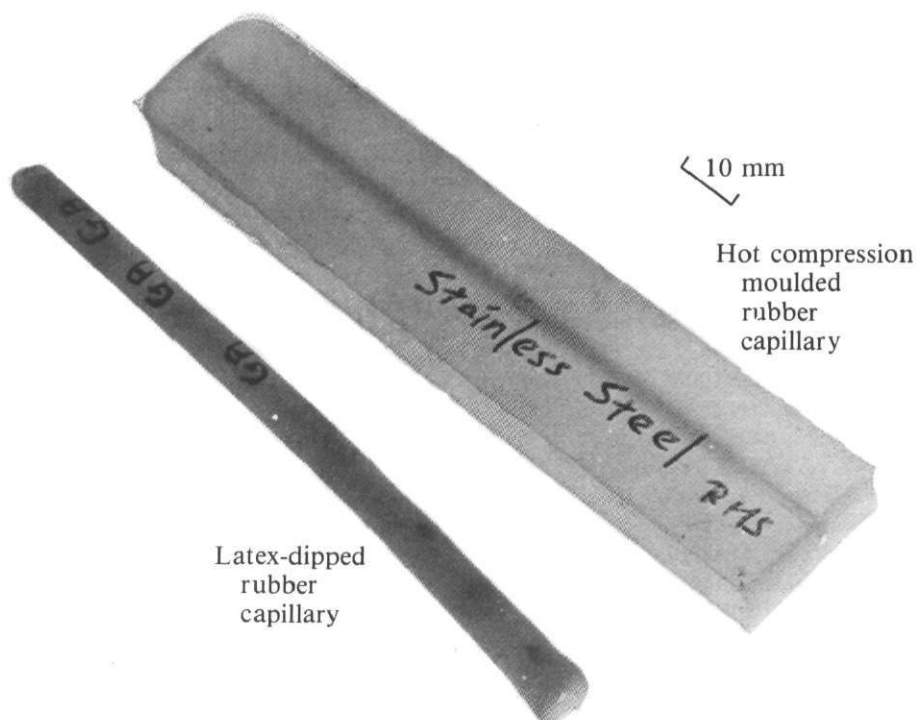


Figure 2. Latex dipped and hot compression moulded rubber capillaries.

potential measurements. They were fitted to the electrode compartments *via* a 2 mm bore glass tube (o.d. 3 mm) of some 4–5 mm in length. The effective length of the rubber capillary was 112 mm.

Capillaries of synthetic rubber were prepared by hot compression moulding, in a similar way to that employed by Lewis¹². The rubber was cold milled with curing agent (2.5% dicumyl peroxide) and sheeted out. A portion was then placed into a small steel frame mould and compressed at 100°C for a few minutes. The mould was then opened and the block of 4.5 mm thick rubber, as yet uncured, was removed. A groove was cut into it and a clean former of glass rod or steel tube placed in the groove. The glass was borosilicate glass (1.5 – 1.8 mm diameter) and the steel was stainless steel (1.6 – 1.8 mm diameter). The rubber block was replaced in the mould, a further 4.5 mm uncured rubber sheet was placed on top, pressure was re-applied and vulcanisation was completed at a temperature of 160°C for 50 min. To remove former rods, the resultant 9 mm thick rubber block was soaked in distilled water at 60°C–70°C for 8 h, whereupon it could be withdrawn to leave a well-formed rubber capillary (*Figure 2*). After cutting to length and drying, this was directly used in the streaming potential apparatus.

Electrical

The cell constant C of a rubber capillary was determined using 0.01M KCl solution. The resistance of the capillary filled with the solution was measured with a high input impedance digital electrometer (Keithley 616, impedance $> 10^{14}\Omega$, resistance mode accuracy $\pm 0.5\%$). Electrical connections to the cell were reversed and the mean of several readings was taken. Resistance values were high ($> 10^5\Omega$) but very consistent, polarisation being negligible. The cell constant was calculated using the literature value for the specific conductance of 0.01M KCl. The potential difference developed across the cell during electrolyte streaming was also measured with the same electrometer but using it in its voltmeter mode of operation (accuracy $\pm 0.2\%$). The resistance of the test electrolyte

(0.001M KCl) in the capillary was also measured ($> 10^6\Omega$).

In the course of carrying out tests, the cell electrodes were kept electrically shorted using a high impedance switch, except when making potential measurements. Data readings were taken when the electrolyte levels in both round-bottom reservoir flasks (*Figure 1*) were about the same.

Potentials were recorded for electrolyte flow in both directions and the average could be taken. Slopes of E/P in either flow direction were always the same (*Figure 3*). When the electrolyte was stationary the typical background potential was 0 to 3 mV, and an allowance was made for this. It is often referred to as the asymmetry potential¹⁴ of the electrode pair.

Referring to *Equation 3*, the values of E/P were derived from the slope of an experimental plot of the variation in the streaming potential E with the applied pressure P . It was sometimes observed that the slopes E/P varied according to whether the applied pressure was being increased or decreased, so under these circumstances averages were taken. The observation suggests that the surface charge on the capillary is changing. It was found that if the electrolyte solution was left in contact, including flushing, with the capillary surface for at least a couple of hours, this variability with pressure was minimised or even eliminated. This hints at surface conditioning.

Electrolyte Solutions

The aqueous electrolyte solution used was 0.001M potassium chloride (analytical grade) made up in conductivity water ($< 0.5 \mu\text{S}$). This was pH adjusted with 0.1M KOH to raise the pH, or 0.1M HCl to lower the pH. Values of pH of the resulting test solutions were determined with a meter, type PHM 64 (Radiometers, Copenhagen).

Test Procedure

All streaming potential measurements were made at a constant temperature of $20^\circ\text{C} \pm 0.5^\circ\text{C}$, achieved with the apparatus situated in a

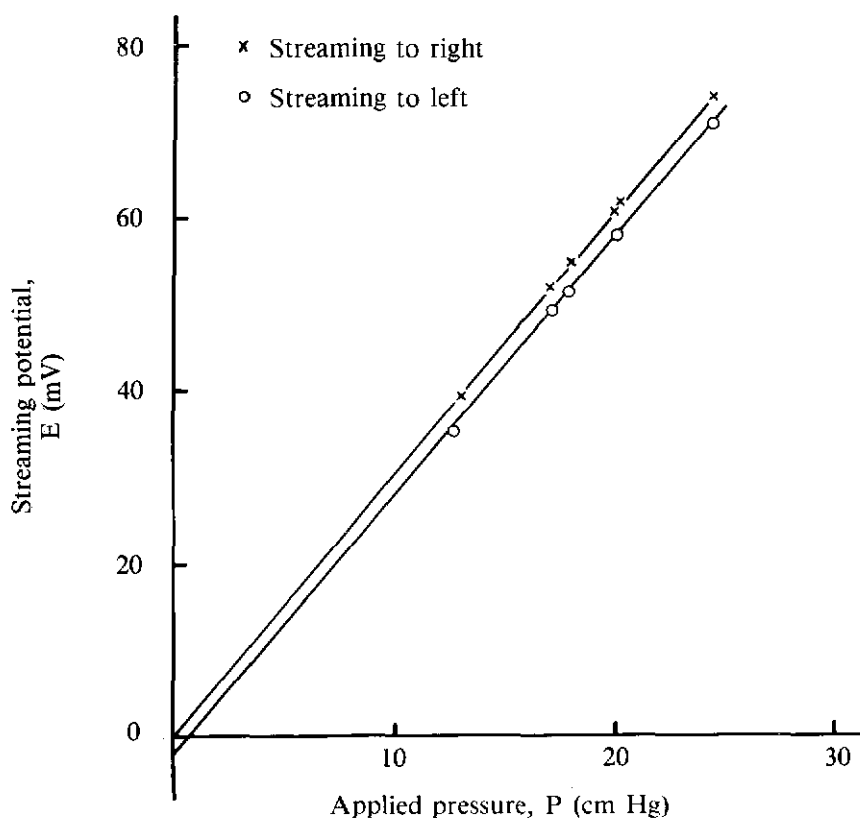


Figure 3. Streaming potential variation with applied pressure for high-ammonia latex capillary filled with 0.001 M KCl.

temperature-controlled laboratory. A problem concerning electrical screening of the apparatus arose. A Faraday cage which was made was found not to be particularly effective. The best situation was to minimise movement of people around the laboratory. By taking these precautions, fairly reproducible streaming potential data were eventually obtained. As a further refinement, pH values of test electrolyte solutions were measured after the experiments to check their consistency.

RESULTS

Natural Rubber Capillaries from High-ammonia Latex

Streaming potential measurements for this type of capillary prepared on a glass former are

shown (Figure 3) as a function of the pressure applied to the electrolyte solution flowing through the capillary. The gradient of the line through the data points gives a value for the *zeta* potential according to Equation 3.

Measurements were made of the *zeta* potential when pH of the electrolyte solution was varied over the range 3.6 to 10. The results shown (Figure 4) for a freshly-prepared capillary reveal a considerable dependence upon the pH of the electrolyte. It was observed that on long contact (six days) with the electrolyte, including flushing, the level of the *zeta* potential fell at high pH accompanied by a small shift in the iso-electric point (Figure 4). This suggests leaching out of charged materials from the rubber surface. Changes in charge level with time have been observed for glass¹³ and other materials¹⁴.

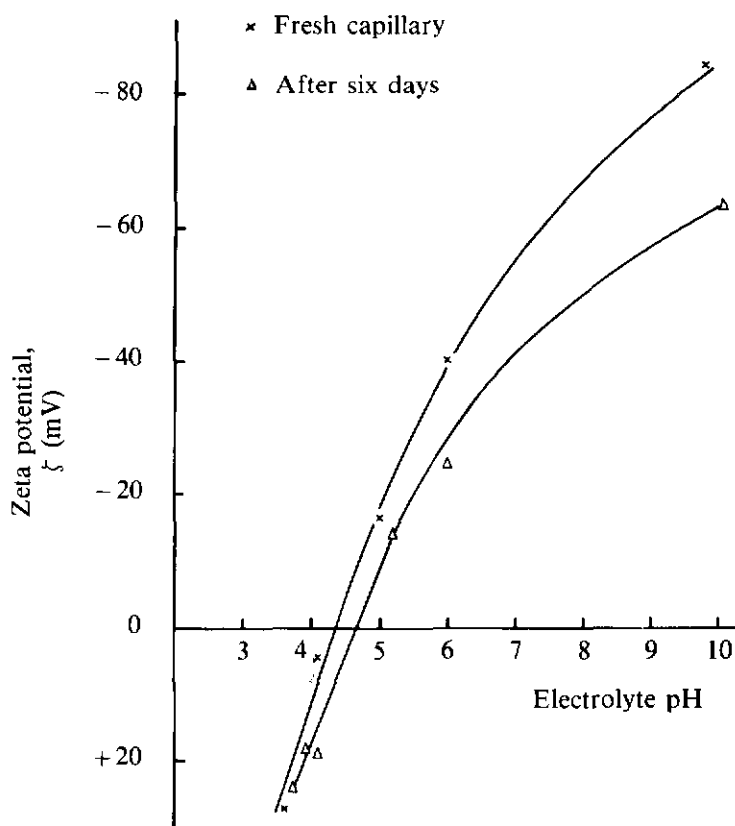


Figure 4. Zeta potential variation with pH of electrolyte solution for HA latex capillary.

The iso-electric point obtained from the data graph for the fresh capillary (Figure 4) is found to be 4.4, which may be compared^{7,8} with the iso-electric point of latex particles of around 3.8–4.6. The closeness of these figures for a solid rubber surface and rubber particles of colloid dimensions is encouraging.

Low-ammonia Latex Capillaries

Experiments similar to those described above were carried out using LA latex and a glass former to prepare rubber capillaries. The zeta potential results were similar to those for HA latex, but shifted slightly in the direction of lower pH. The LA latex capillary had an iso-electric point of 4.0.

Low-nitrogen Natural Rubber Capillaries

A sample of HA latex (0.3% N) was treated with a proteinase (Novo SP 88), stabilised with non-ionic surfactant (Texofor FN 30) and washed by repeated centrifuging and dilution. Its nitrogen content by weight was then reduced to 0.04%. The so-prepared latex was used to make rubber capillaries (four thin coats of DP latex plus four thick outer coats of prevulcanised Revultex HR latex). A zeta potential/pH curve was obtained from streaming potential measurements and found (Figure 5) to be similar to that for HA latex (Figure 4). The iso-electric point was 4.3.

The fact that the zeta potential results for low nitrogen and HA latex materials were similar

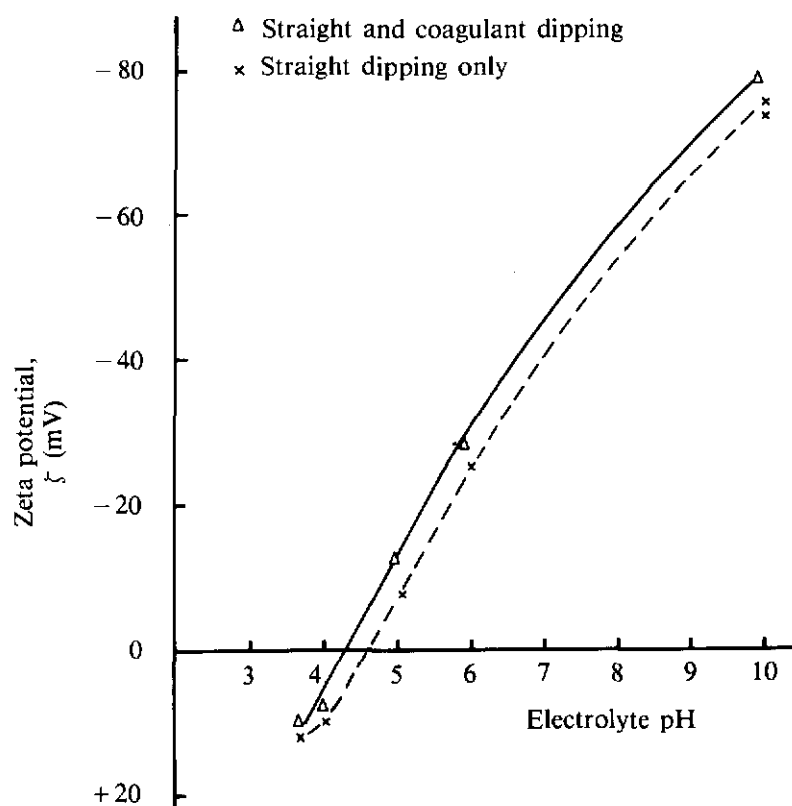


Figure 5. Zeta potential variation with pH of electrolyte solution for deproteinised capillaries prepared by straight and coagulant dipping and straight dipping only.

was surprising. When the materials as latex particles were compared by moving boundary electrophoresis, the low nitrogen sample had about half the mobility of the HA latex sample. A possible reason for the discrepancy in the streaming potential measurements on solid surfaces may be due to short chain charged species caught at, or migrating readily to, the solid surface.

It was conjectured that a possible source of migrating proteinaceous material might be the prevulcanised (0.3% N) outer layers of the capillary (see *Experimental*). To answer this surmise, another capillary was prepared consisting of some fifty thin coats of deproteinised rubber with no outer coats of prevulcanised latex. This capillary when tested showed (Figure 5) only slightly lower potential values

at higher pH values. The similarity in zeta potential levels of HA and DP rubber, despite different bulk nitrogen contents, remains to be explained.

Synthetic Rubber

A few capillaries were prepared from Natsyn (synthetic equivalent of natural rubber) by hot compression moulding using glass and steel rod formers (see *Experimental*). Results for the variation in zeta potential with pH show (Figure 6) that for freshly-prepared samples there is a difference in potential level according to the type of former, that for glass being noticeably higher. However, after soaking in electrolyte including flushing, the observed potential for the glass former type decreased appreciably. This may be compared with the

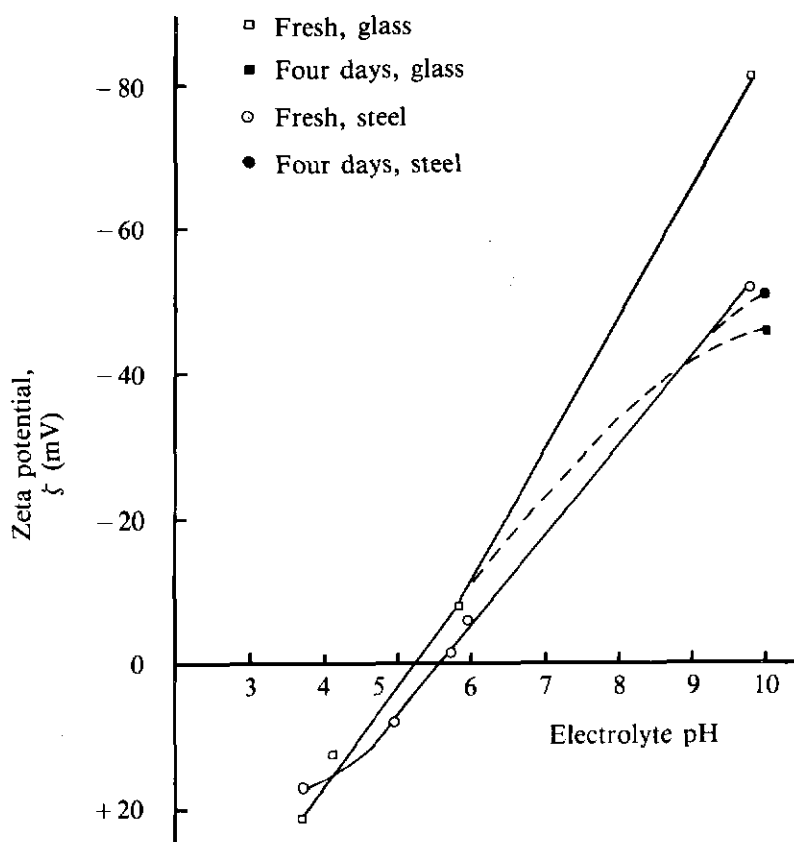


Figure 6. Zeta potential variation with pH of electrolyte solution for Natsyn rubber capillaries prepared on glass and steel formers.

steel former type that did not give a changed potential after soaking and flushing with electrolyte. This suggests residual charged species imprinted onto the rubber by the glass former that are reasonably soluble and which eventually become flushed away.

It will be noticed from Figure 6 that the iso-electric point for the steel former type is 5.6, whereas that for the glass type is 5.2. The synthetic rubber, Natsyn, contains catalyst residues and the dominant element present is titanium in the form of its oxide (Table 1). The iso-electric point¹⁴ of TiO_2 is 5.8. This is near to the measured value (Figure 6), suggesting that it is the catalyst residue in the capillary

TABLE 1. ANALYSIS OF RUBBER

Major metallic elements (p.p.m.)	NR (HA)	Natsyn 2200	IR-305
Aluminium	6.3	340	24
Calcium	2.9	15	12
Iron	5.2	15	10
Lithium	0.05	0.07	3.4
Magnesium	6.7	6.9	15
Phosphorus	550	10	—
Potassium	108	22	Trace
Silicon	1.5	560	196
Sodium	12	23	13
Titanium	9.4	5 700	1.4

surface that helps to determine the rubber's surface charge and iso-electric point. In the case of the use of a glass former which may imprint siliceous material onto the capillary surface, the iso-electric point^{12,14} of silica/glass is in the range 2 to 4 depending on the type, which may account for the shift to iso-electric point 5.2 for this type of capillary (Figure 6). Furthermore, Lewis¹² had reported that the synthetic rubber Cariflex IR305 was used and the iso-electric point was 3.4. The dominant residual element in this rubber is silicon. This may be present as silicate or silicone. However, there is indication that siliceous material from the glass former may be deposited on the capillary surface and this would determine the iso-electric point and surface charge characteristics of Cariflex IR305. This may explain the difference in iso-electric points between Natsyn and Cariflex.

An important point to note about Natsyn is that potential levels are generally lower than for natural rubber (compare Figures 4 and 6). This may reflect the absence of proteinaceous material and higher fatty acids in Natsyn.

DISCUSSION

The experimental investigation herein reported shows that *zeta* potentials can be measured satisfactorily by streaming electrolyte through a rubber capillary. Reasonable values of potential are produced and, indeed, the observed iso-electric points agree closely with those determined using latex particles. Although making streaming potential measurements on rubber capillaries is relatively simple, the method appears sensitive to surface residues such as proteins, soaps and minerals.

A noted influence on potential values was the electrolyte pH. This is reminiscent of the wet friction¹⁵ response of raw rubber to lubricant pH. In that investigation¹⁵, it was found that the friction decreased with increasing electrolyte pH by a factor of about three over the pH range 2 to 11. The present investigation shows that over this pH range the *zeta* potential undergoes a sign reversal from being positive to strongly negative at high pH. There would appear to be

a link between wet friction and *zeta* potential, perhaps through the mechanisms of electrical double-layer repulsion^{12,16,17} and steric hindrance¹⁸.

Another influence on potential values was the type of former employed to make a rubber capillary, whether glass or stainless steel. There was also the observation of a decrease in potential with repeated flushing of a capillary by electrolyte over a number of days. The inference is the removal of soluble charged species. The implications of this and other factors with respect to latex stability must await further study.

CONCLUSION

From the results of this investigation, we conclude that the method of streaming electrolyte solution through a rubber capillary is simple and yet yields useful data. It could become a method of characterisation for solid rubber surfaces. There are likely to be other applications, such as in the understanding of some of the complexities of the stability of rubber latex.

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