

Experiments on the Lubrication of Raw Natural Rubber

E.L. ONG* AND A.D. ROBERTS**

The surface lubrication of a few grades of raw natural rubber (NR) was investigated with simple friction apparatus. Various liquids at room temperature were used. In particular the effect of aqueous solutions of inorganic salts, lipids and rubber protein was examined.

The 'tackiness' of raw rubber can be reduced by liquid or solid lubricants and also by surface chemical attack such as chlorination. This is important in rubber manufacture. The way liquids lubricate raw rubber is of wider interest in unvulcanised rubber products, such as shoe sole crepe, adhesives and plastics modifiers, and has a bearing upon the mechanical stability of rubber particles in latex. While much has been published on the lubrication of vulcanised rubber, there appears to be little published information on raw rubber. We report experiments on the lubrication of standard grades of raw Malaysian rubber by hydrocarbon liquids and thin films, inorganic solids, soap and aqueous solutions of inorganic salts and rubber protein.

EXPERIMENTAL

Rubber samples were designated grades of Standard Malaysian Rubber (SMR) and were compression moulded into smooth-surfaced hemispheres¹. Friction measurements, used to indicate the efficacy of a lubricant, were made with simple apparatus¹. A raw rubber hemisphere was drawn over a flat track of 'Perspex' (polymethylmethacrylate) in the presence of the lubricant under test. The 'Perspex' track was selected as the contact interface could be viewed directly through the 'Perspex' plate¹ but there was no provision for measuring lubricant film thickness between surfaces. In some tests, for symmetry, the track surface was

the same rubber (thin sheet) supported by the 'Perspex' track. Under a normal load, W , the sliding friction force, F , was measured at a given speed and the friction coefficient, $\mu = F/W$, used as a comparison for different lubricants. Unless stated otherwise, the 'Perspex' track surface was solvent cleaned by wiping with tissue paper moistened with isopropanol, and allowed to dry. All rubber surfaces were tested as moulded without solvent treatment.

RESULTS

Contaminant Films

In an earlier communication¹, it was noted that the presence of trace amounts of surface contaminant, such as silicone release agent, could reduce the sliding friction of raw rubber by up to 50%. A raw rubber hemisphere 'as moulded' generally has a dry friction coefficient greater than 3. Surface cleaning of it with solvents (impregnated cotton wool wipe and allow to dry) can cause an increase in the friction, and if the hemisphere is extracted in cold acetone (frequent changes of acetone over a period of a month) it is found that the friction increases further (*Table 1*). This suggests that solvent wipe cleaning of rubber surfaces removed some low molecular weight materials that act as a boundary lubricant, and longer term soaking in solvent removed more of them. This interpretation may, however, be complicated by residual solvent left after drying that

*Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia

**Malaysian Rubber Producer's Research Association, Brickendonbury, Hertford, SG13 8NL, United Kingdom

TABLE 1. EFFECT OF SURFACE CONTAMINANTS ON FRICTION

Surface condition	Friction coefficient	Observations
Rubber 'as moulded'	3.1	Ridge ¹ formed during sliding
Rubber surface cleaned with acetone	3.3	No colouration on wipe tissue
Rubber extracted in cold acetone	5.7	Acetone acquires brownish colour
Cast film of NR extract — prolonged running	0.9 0.1	No ridge or surface damage
Rubber, covered with NR extract, re-run on clean track	0.7 2.0	Initial friction later rises with damage to surface

SMR CV hemisphere (R = 21 mm) sliding at 0.2 mms⁻¹ on smooth 'Perspex' track under 1.57 N load, temp. 23°C–24°C, RH = 55% – 65%. Friction coefficients quoted are averaged values; the scatter was about ±20%

softens the rubber leading to more intimate contact and a higher friction.

The lubricating effect of materials extracted by acetone from raw rubber (RSS 1) was examined. The acetone extract was evaporated down and solids were re-dissolved in ethanol (necessary because acetone attacks 'Perspex') then cast from the solution as a dry, thin surface film on a smooth 'Perspex' track. A clean raw rubber hemisphere was drawn over the extract film. The friction was initially high, but fell with prolonged running to a low order (*Table 1*); a sliding mark was left in the surface film, but there was no damage to the rubber which had acquired a waxy surface appearance after this test. Materials from the cast film became transferred onto the rubber, eventually in sufficient quantity to greatly reduce the friction. Whenever the waxy surfaced hemisphere was re-run (without solvent cleaning) on a new area of cast film, the friction remained low, but when it was re-run on a clean area of 'Perspex' track (no cast film present) the friction rose with increasing sliding distance to a high value (*Table 1*). With increased friction, there was some damage to the rubber surface. The waxy material on the rubber hemisphere appeared to be wiped away by sliding against the clean track, and this may always happen to trace contaminants on a raw rubber surface during sliding.

Solid Lubricants

In manufacturing operations the dusting of rubber with talc is extensively employed to reduce tack. The effect on the friction of raw rubber was examined. An unvulcanised rubber hemisphere was lightly dusted with talcum powder and then run dry against a clean 'Perspex' track. The friction was about half that of an untreated 'as moulded' hemisphere (*Tables 1 and 2*). If water was added to the contact region the friction fell considerably, or alternatively if a liberal amount of talc was added (*Table 2*). It was clear that a range of friction values could be obtained depending upon the amount of talc present, and this can be exploited in practice, for example, to obtain just the right amount of interply tack in latex thread.

Magnesium oxide powder (coarse particles) was dusted liberally onto a raw rubber hemisphere and the sliding friction measured against a 'Perspex' plate. There was surface damage of the rubber. After repeat testing it appeared that the friction coefficient was very considerably higher (*Table 2*) than for a liberal dusting with talc. This presumably reflects the difference in shear properties of the two powders.

In practice, the tack of rubber articles is often reduced by surface chlorination. The

TABLE 2. SOLID LUBRICANTS OF RAW RUBBER

Treatment	Friction coefficient	Observations
Slight dusting with talc — water added	1.7 - 2.4 0.01	Rubber slightly scuffed No surface damage to rubber
Liberal amount of talc	0.01	No damage
Magnesium oxide powder	1.7 - 2.3	Rubber surface damaged
Surface hypochlorination	0.3 - 0.5	Surface whitening but no gross changes
Sulphuric acid attack	0.4 - 0.5	

SMR CV hemisphere ($R = 21$ mm) sliding at 0.25 mms⁻¹ against smooth 'Perspex' under 1.57 N load, temp. 23°C - 28°C , RH = 55% - 80%

surface of a raw rubber hemisphere was treated with 0.3% aqueous chlorine solution (3 min immersion; followed by neutralisation with 10% ammonia, washed and dried). After chlorination the surface was slightly whitish. The dry sliding friction against smooth 'Perspex' was now (Table 2) nearly an order of magnitude less than an 'as moulded' hemisphere, and there was no surface damage done to it. Another hemisphere was treated with a few drops of concentrated sulphuric acid (3 min; then ammonia neutralised, washed and dried). Again a whitish surface resulted and the sliding friction was much reduced (Table 2). Sulphuric acid is used in industry to reduce the tack of unvulcanised rubber. The reduction in friction by both chemical agents is probably mainly brought about due to physical roughening of the rubber surface.

A comparison of the changes in surface texture due to chlorination for different immersion times (Figure 1) was made by Scanning Electron Microscopy (SEM). At 2 min immersion a 'domain' pattern becomes etched into the surface on a scale of 5 - 10 μm . After 8 min the domains are lost and a 1 μm particulate structure prevails. These textural changes will lead to a loss of real contact against a hard substrate (track). They explain why the friction falls, without having to invoke uncertain arguments about the changed chemical state of a treated surface. A further feature of chemical treatment is a hardened skin. The higher surface elastic modulus means less material comes into real contact with the substrate for a given

applied load. Thus two factors, surface roughness and hardness, conspire to reduce tack and sliding friction as a consequence of surface chlorination.

Sulphuric acid treatment also renders the rubber surface more rough and hard. SEM analysis, however, shows in this case no domain structure. After 3 min contact with sulphuric acid a fine particulate texture appears, on a scale 0.1 - 0.2 μm . Again, it is clear why the friction falls with this treatment.

Electron probe analysis of chlorinated SMR CV surfaces was carried out, using chlorobutyl rubber as a standard. After 2 min immersion in chlorinating solution it was found that approximately 2.2% Cl was retained in the SMR surfaces; at 4 min and 8 min the levels were 3.3% and 5.2% . It was discovered that by fracturing rubber samples cooled in liquid nitrogen, a sufficiently clean fracture could be obtained to allow a cross-sectional chlorine profile to be made. The chlorine penetration depth for a few minutes immersion in chlorination solution was typically 25 μm .

A similar electron probe procedure using a sulphur standard indicated that after 3 min contact with sulphuric acid about 2% S was retained in an SMR CV surface.

Lubrication by Soap

Different amounts of the detergent 'Teepol' (mixture of soap, the main one being sodium dodecyl sulphate) were deposited in different



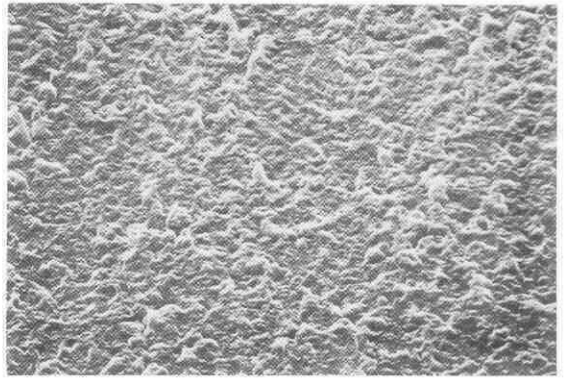
Untreated



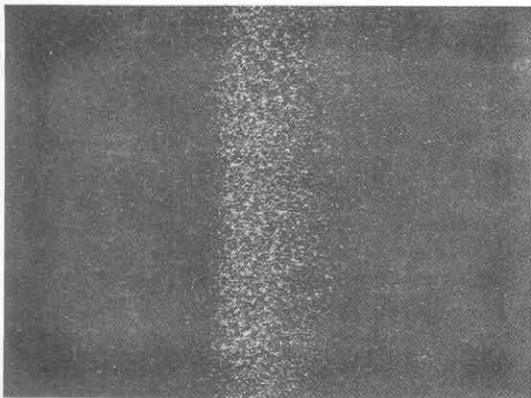
2 min immersion



4 min immersion

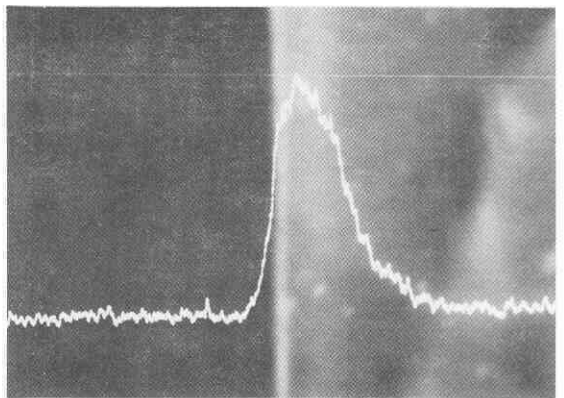


8 min immersion



Cl x-ray map

2 min immersion



Cl level

2 min immersion

Figure 1. Surface of SMR CV after chlorination. Magnification: 800 ×.

ways on the 'Perspex' track and the lubricating effect observed (*Table 3*). The results demonstrate that Teepol can be a most effective lubricant. In the presence of Teepol, sliding damage to the rubber surface was usually reduced to a negligible amount, although for dilute aqueous solutions a certain conditioning time appeared to be necessary to achieve the lowest friction with least damage.

In rubber processing, stearic acid and stearates function mechanically as lubricants to reduce die drag, aid milling, act as mould release agents and to improve knitting. In the present tests, they were deposited as thick films from alcohol onto the 'Perspex' track and the friction of a raw rubber hemisphere measured in their presence. As dry boundary lubricants at room temperature, they just about halve the friction compared to clean surfaces, but when water was added to the stearates they lubricated more effectively, presumably due to the action of an aqueous soap film despite their sparing solubility in water. The ammonium salt is more soluble and gave the lowest friction when water was added.

In view of the good lubricating action of the detergent 'Teepol' the action of a non-ionic surfactant was also examined. A drop of 'Triton X-100' (iso-octylphenoxy polyethoxyethanol)

was added to 20 ml of water and the solution spread on the 'Perspex' track. A rubber hemisphere (SMR CV) was drawn over the track at 0.25 mms^{-1} under 1.57 N load. There was no damage to the rubber surface and the friction coefficient was 0.01 or less, no conditioning time being required to reach this low friction. After the test, the sliding surfaces were thoroughly rinsed with water, the rubber cleaned with acetone and then the friction was re-measured with distilled water as lubricant. The friction coefficient was 0.7 - 1.6 (stickslip), suggesting that most of the Triton X-100 had been removed. Clearly, the Triton is a good lubricant of raw natural rubber and it appears to act immediately.

Action of Various Liquids

Raw rubber hemispheres were pulled across the 'Perspex' track in the presence of liberal amounts of various liquids at room temperature. Friction values varied widely (*Table 4*). Both water and glycerol appeared to be poor boundary lubricants, as judged by the high 'stick' value of the sliding stickslip motion. During the slip, the friction fell towards zero. The impression gained was that the rubber moved rapidly ($\sim 1 \text{ ms}^{-1}$) when slipping and at this moment both liquids were good hydrodynamic lubricants. The slightly lower stiction

TABLE 3. LUBRICATION OF SMR CV BY SOAP

Track treatment	Friction coefficient	Observations
16% aqueous Teepol	0.01 (av)	2 min conditioning time
Thin smear	0.1 (av)	Friction falls with Teepol pickup
Thin 'invisible' film	0.4 - 1.8	Surprisingly effective
Ammonium stearate film — water added	1.7 - 2.0 0.06	Some damage to rubber No damage
Zinc stearate film — water added	1.3 - 2.0 0.6	Rubber surface damage Only slight scuffing
Stearic acid film — water added	1.5 - 2.2 0.8 - 1.1	Rubber surface damage Stickslip and scuffing
Clean, dry surfaces	> 3	Gross damage to rubber (ridge deformed)

Rubber hemisphere (R = 21 mm) against 'Perspex' track; normal load 1.57 N, temp. = 24°C, sliding speed 0.25 mms^{-1}

TABLE 4. LUBRICATION BY VARIOUS LIQUIDS

Liquid	Friction coefficient	Observations
Distilled water	2.7 (max)	Severe stickslip, rubber scuffed
Glycerol	2.1 (max)	Stickslip
Ethanol	1.2	Steady sliding, no marked damage to rubber surface
Isopropanol	1.5	
Dutrex oil	2.1	
Viscous silicone	0.03 - 0.06	Micro-stickslip
Silicone emulsion	1.9 - 2.4 (max)	Severe stickslip

SMR CV hemisphere ($R = 21$ mm) sliding at 0.25 mm^{-1} on smooth 'Perspex' track under 1.57 N load, temp. 23°C - 24°C , RH = 55%-65%

value for the glycerol may reflect its lower surface tension (63 mJm^{-1} at 25°C).

Ethanol and propanol were better lubricants and this may in part be due to their low liquid surface tensions (21 mJm^{-1} - 22 mJm^{-1}). With both, the sliding motion was steady. The slightly higher friction with isopropanol may be due to its viscosity being twice that of ethanol. Dutrex oil is more viscous and an even higher friction was observed.

Two types of mould release agent were examined, one consisting of a viscous silicone fluid dissolved in a volatile solvent (Bomb-Lube, Addison Chemical) and the other a silicone fluid-in-water emulsion (Shell Chemicals). With the first type the volatile solvent was allowed to evaporate and then the 'Perspex' track was lubricated with the residue; with the second type the track was directly lubricated with the emulsion. Both were tested at room temperature and the results were very different. With the first, the silicone residue was an effective lubricant, but the second showed the same behaviour as lubrication by distilled water, though stiction was less severe. If the second type was used in practice on a hot mould, water would evaporate off and its lubrication behaviour would approach that of the first type.

Aqueous Electrolytes

Various investigations²⁻⁴ have shown that salt solutions can lubricate vulcanised rubber better

than distilled water, but the observations do not support any single concept as to why this is so. The effect on *raw* rubber friction was tested by sliding hemispheres of unvulcanised rubber (SMR CV) over the 'Perspex' track flooded in turn with different salt solutions in water. The investigation also encompassed their effectiveness for rubber-rubber contact. The results (Table 5) show an effect of both the actual salt employed and the nature of the contact surfaces. Further data for rubber-'Perspex' contact indicates an effect of concentration (Figure 2).

Lipids and Proteins

There is ample evidence⁵ of the presence of lipids and proteins in the surface layer around rubber particles in fresh field latex. The following experiments were performed to examine their possible role in lubrication mechanisms.

The polar lipid lecithin (phosphatidyl choline) is believed to be present around particles of rubber in latex. For our experiments lecithin from egg yoke was used (BDH, 33%). Chemical analysis of the sample showed it to be partially hydrolysed, a variety of phospholipids being present e.g. phosphatidyl choline, phosphatidyl serine, phosphatidyl inositol, and phosphotidic acid. A dilute ethanol solution ($>0.5\%$) was prepared from which a thin lipid film was deposited onto the 'Perspex' track. This cast

TABLE 5. LUBRICATION BY AQUEOUS SALT SOLUTIONS

Lubricant	Friction coefficients	
	'Perspex'/rubber	Rubber/rubber
Dry surfaces	4.1	10
Distilled water	2.6	7.4
Sodium nitrite	2.6	7.3
Sodium sulphite	2.1	4.9
Sodium chloride	1.5	4.6
Sodium carbonate	1.1	2.1

Normal load 3.43 N, sliding speed 0.2 mms^{-2} , temp. = 22°C – 24°C , RH = 55%–65%. SMR CV hemisphere ($R = 21 \text{ mm}$) slid on smooth 'Perspex' track or on smooth sheet of SMR CV (5 mm thick) supported on the 'Perspex' track. All salt solutions were 0.1M concentration. Stick-slip motion tended to occur and maximum friction coefficients are quoted.

film consisted of both neutral and polar lipids on the approximate ratio 10:1 respectively. Neutral lipids present were monoglyceride, diglyceride, triglyceride, free fatty acids and sterols. A raw rubber hemisphere (SMR CV) was drawn over the cast film when dry. A

friction coefficient value of 1.8 was typical; no ridge formed on the rubber but there was some slight surface damage. A plough mark was left in the cast lipid film and some of the lipid became transferred onto the rubber surface. When the track was flooded with distilled water

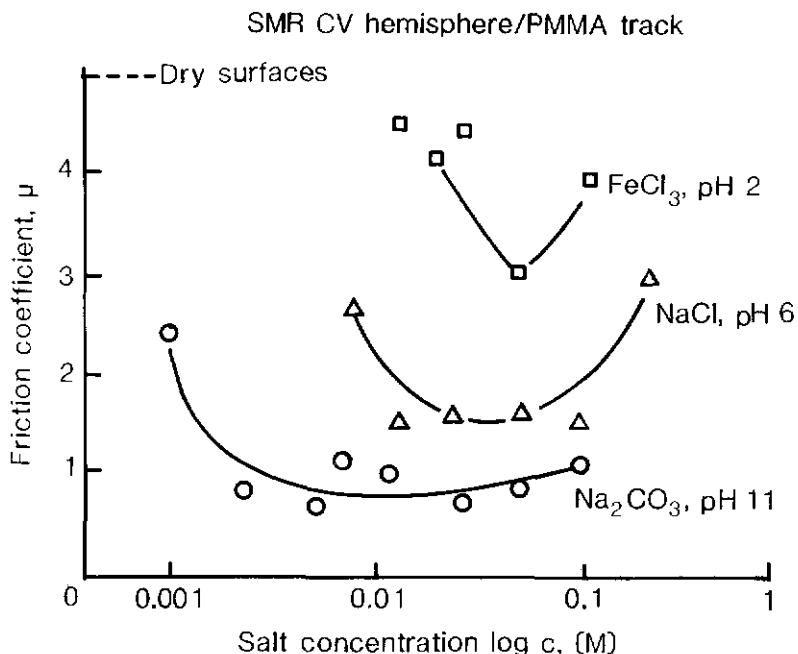


Figure 2. Effect of salt solutions on friction. (Sample was acetone-extracted SMR CV whose dry friction coefficient was 5.1.)

the friction fell considerably, so suggesting enhanced lubricating action in the presence of water (Table 6).

The neutral lipid, tristearin (99% pure sample) was friction tested in a similar manner. A film of it was cast from hexane solution onto the 'Perspex' track, the film obtained being powdery. In dry sliding contact with a raw rubber hemisphere the friction was rather high, there was transfer of the tristearin onto the rubber but no apparent damage to its surface. When the track was flooded with water the friction fell to a low value, although the water did not wet (water beads) the tristearin coated track (Table 6).

A sample of freeze-dried C serum* was made up to a 6% by weight aqueous solution and this was spread on the 'Perspex' track. A rubber hemisphere (SMR CV) was drawn over the track. The friction coefficient varied around 0.9 and the rubber surface was slightly damaged. For comparison the dry friction coefficient for clean dry surfaces was greater than 3, and so the serum appeared to provide a degree of modest lubrication.

Surface protein can be extracted off rubber particles. A solid sample was made up into aqueous solution by dissolving 10 mg in 2 cc of borate buffer solution (pH = 8.9). The

'Perspex' track was lubricated with the aqueous solution and a rubber hemisphere (SMR CV) drawn over it. On the first pass, the friction coefficient was 0.9, but on the second pass made a few minutes later the coefficient was 0.006. This suggests a conditioning effect; presumably the protein requires time to absorb to the sliding surfaces. The friction coefficient with borate buffer alone was 1.7. Thus it would appear to be the protein (or any contaminants it may contain) that provides for good lubrication.

For comparison, another protein solution was used as lubricant. The 'Perspex' track was flooded with a 1% aqueous solution of casein and the rubber hemisphere drawn over it as before. On the first run the friction coefficient was 0.31 - 0.28 (falling with increasing displacement), and by the third run it had steadied to 0.18. There was no surface damage to the rubber. It appears that this protein can also act as a lubricant in aqueous solution, though it is not as effective as the rubber particle protein solution.

DISCUSSION

The foregoing experiments represent an attempt to explore broadly how the friction of raw natural rubber is altered, if at all, by the presence of different liquids and solids that

TABLE 6. LUBRICATION BY LIPIDS AND PROTEINS

Material	Dry friction coefficient	Wet friction coefficient
Mixed lipids Neutral lipid/Polar lipid 10:1	1.6 - 2.5	0.3 - 0.4
Tristearin	1.1 - 1.7	0.2
NR latex C serum		0.7 - 1.1
NR surface protein		0.006
Casein		0.18

SMR CV hemisphere (R = 21 mm) sliding at 0.2 mms⁻¹ on smooth 'Perspex' track under 1.57 N load, temp. 24°C-26°C, RH = 60%-70%

*The ambient serum around the rubber particles in latex that contains 15% or more of protein plus smaller amounts of carbohydrates and organic acids.

might be expected to act as lubricants. 'Soapy' liquids and 'flakey' solids gave the most dramatic results. Detergent solutions, such as sodium dodecyl sulphate, were able to bring about a hundred-fold drop in the level of friction, as was talcum powder; the former probably because of boundary action² and the latter due to its solid lamella structure.

Less spectacular changes were brought about by contaminant films of organic substances. For example, at room temperature a film of stearic acid could barely halve the value of the dry friction. Stearates were a little more effective, particularly in the presence of water if they were sparingly soluble. Presumably, this is due to boundary action akin to aqueous detergent films, such as electric double-layer repulsion and, or, steric hindrance. This may be compared with distilled water that is a poor lubricant at low sliding speeds, though improved by dissolving certain salts in the water. Any trapped water film in the contact zone probably collapses rapidly, so leading to high interface adhesion and friction. Some salts and soap can help to resist the collapse. The lubricating ability of hydrocarbon liquids was not much better than that of water, any improvement probably reflecting a lower surface tension or higher bulk viscosity.

An intriguing aspect of lubrication by aqueous salt solutions was the change in efficacy with the actual salt employed, and with its concentration. It has been observed in studies of the lubrication of fully vulcanised rubber that some salt solutions can reduce the friction²⁻⁴, and this may be due to the creation of an electrical double-layer on both contact surfaces. The mutual electrostatic repulsion is enough to reduce the friction. Detailed interpretation is complicated by the surface characteristics of the contacting bodies. Any mutual repulsion (or attraction) can in part arise from chemical changes at the surfaces, in addition to any adsorbed layer of charge.

The most effective salt lubricants of raw natural rubber were found to be solutions of sodium carbonate and bicarbonate. These are alkaline and one may speculate that if residues

in the contacting surfaces are involved in the lubrication mechanism, then conditions that favour enhanced charge repulsion due to them are more likely to reduce the surface friction. At high pH the protein residues in the rubber are in the charged form $H_2N.Pr.COO^-$. Furthermore, hydroxyl ions may act on the 'Perspex' surface to give the charged species $CH_2 CH_3 C COO^-$.

Support for these charge effects comes from experiments (*Figure 2*) indicating that the friction falls as the pH of a salt solution increases.

The various friction tests carried out on lipids and proteins suggest that they act, in varying degrees, as boundary lubricants of raw rubber. In particular, the protein surrounding rubber particles appears most effective and this may relate to the mechanical stability of latex.

CONCLUSION

Lubrication studies of raw rubber indicate similar trends as for vulcanised rubber. Aqueous soap solutions and certain proteins are excellent boundary lubricants, probably on account of electrical double-layer repulsion and protective adsorbed layers. Liquids containing few or no free ions for example, water, are less effective. Alcohol is a little better and this may be due to its lower surface tension. Oils appear to depend upon viscosity and low surface tension for their lubricating effect. Solid lubricants, such as zinc stearate or talc, act to reduce the adhesion between raw rubber and track so that the friction can be as low as with soap solution. Poor lubricants result in rather more surface damage to raw rubber than would occur to a vulcanisate.

ACKNOWLEDGEMENTS

The authors thank S.J. Tata for specimens of NR surface protein, J.M. Brown and A.J. Cobbold (MRPRA) for SEM observations, and A. Majid and N. Srikanan for experimental assistance.

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