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Influence of Proteinaceous Material on the Sliding Friction of Rubber Against Ice

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The sliding friction of smooth-surfaced cis-*1,4-polyisoprene rubber containing four levels of nitrogeneous material has been measured against polished ice at two temperatures, −4°C and −31°C The measurements were performed using a deep freeze friction apparatus which included facilities to make optical observations of the contact interface during sliding All rubbers used were 2% dicumyl peroxide cured The comparison between the sliding friction values for the four rubber types is most meaningful at low sliding speeds where rubber wear and frictional melting of ice were negligible Results showed that, in general, the sliding friction increases with the nitrogen content of the rubber However on ice at −4°C the results demonstrate that the friction is low and generally independent of the nitrogen content, although skim rubber (highest N-content) showed slightly higher friction at low sliding speeds*

It has already been noted[1] that the addition of skim rubber (obtained during latex concentration) can make a positive contribution to ice traction at low temperatures This observation was based largely on technological assessment using a pendulum skid tester The investigation reported here represents an attempt to look in greater detail at the influence of nitrogeneous non-rubber material on continuous sliding ice friction This involved measurements on a moving circular ice track against which hemispherical rubber test sliders were pressed If the rubber hemispheres were transparent, then interface events could be followed directly by viewing the contact zone In particular, the area of contact could be measured

EXPERIMENTAL

The apparatus used for the measurement of rubber sliding friction against ice has been described previously[2,3] Essentially, the apparatus employs a smooth-surfaced rubber hemisphere in contact with a circular track of polished ice *(Figure 1)* In addition, the nearly circular area of the rubber-ice interface can be viewed through a ×10 telescope while the frictional force is being measured by a load cell, thus allowing not only the detection of physical events such as Schallamach waves, frictional melting and macroscopic wear of rubber, but also the direct measurement of dynamic interface dimensions The ice-track is housed inside a chest refrigerator so that macroscopic frosting of the friction surfaces is virtually eliminated A contact thermocouple is used to continuously monitor the ice-surface temperature

The ice-track used was prepared from distilled water (electrical conductivity of 10^{-4} Sm^{-1}, pH7) which was frozen on a glass turntable *(Figure 1)* Before each friction test, the ice surface was polished by skimming with a clean sharp razor blade this ensured a highly polished, frost-free ice surface, as confirmed by viewing through the telescope, so that meaningful comparisons are possible between the different rubber types.

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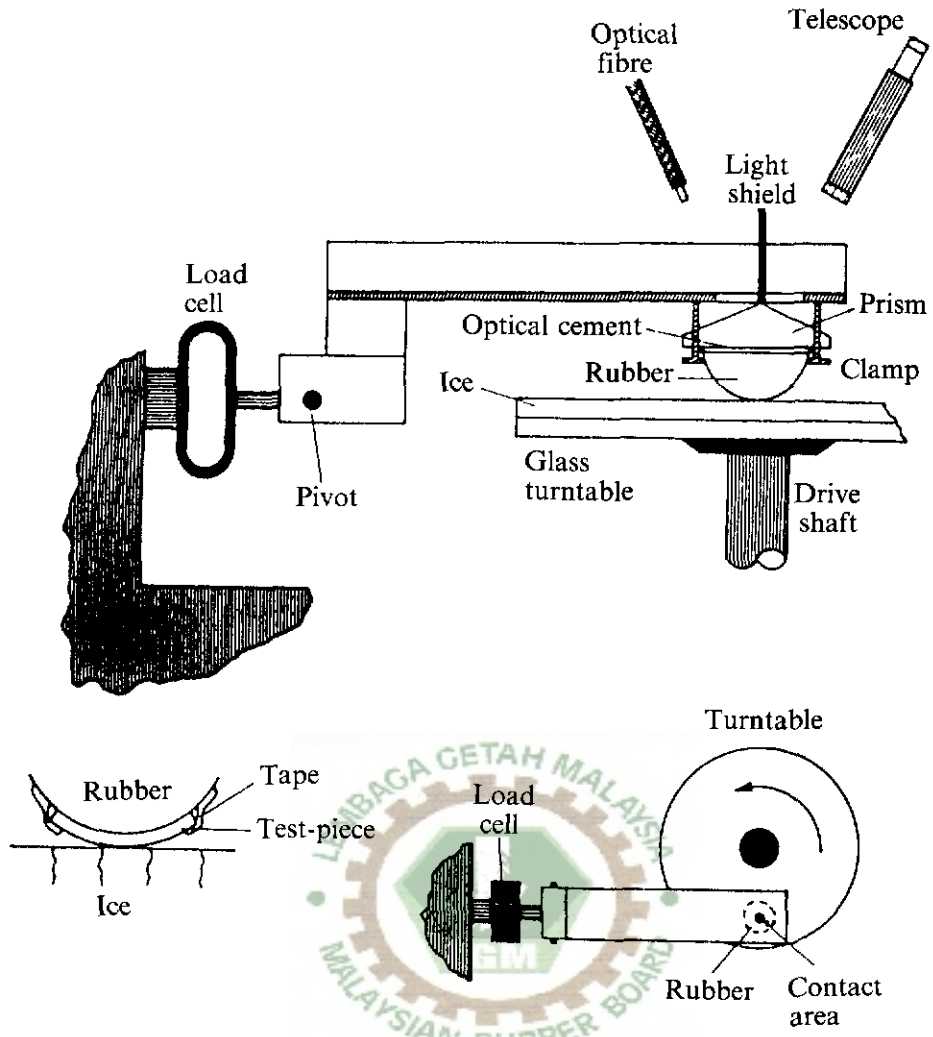

Figure 1. Test apparatus used to study the friction of smooth hemispherical rubber surfaces against polished ice; the apparatus is housed in a temperature-controlled chest freezer (after Ref. 3).

The hemispherical test surface was formed by wrapping a small section of the smooth vulcanisate sheet (3 mm thick) around an optically transparent smooth-surfaced synthetic *cis*-1,4-polyisoprene hemispherical former of radius 18.5 mm. This procedure allowed ready testing of the various rubber types. Before each friction measurement, the smooth rubber surface was cleaned with acetone (Analytical grade)-soaked cotton wool. When the sample rubber had reached the required temperature, it was gently lowered onto the stationary ice track under a load of 5 N and after a dwell time of 30 s, relative motion was initiated. A typical friction trace is shown in *Figure 2*. Direct optical observations through the telescope gave the dimensions of the static and

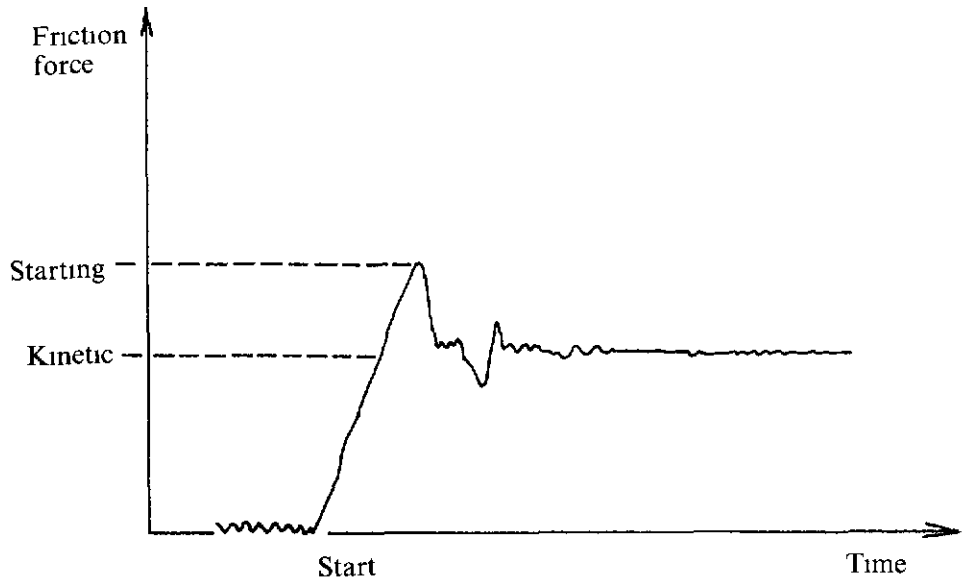

Figure 2 Typical friction trace obtained for rubber sliding on ice

dynamic contact interface (for transparent test-pieces).

Rubber Samples

Four polyisoprene rubbers with differing levels of nitrogenous material were used The nitrogen content of each was determined by the standard Kjeldahl method, the content being related to the protein level A conversion factor for nitrogen to protein content of 6 25 by weight is generally considered to be acceptable. The rubbers used and how they were formulated are shown in *Table 1*

The sliding friction of the four smooth gum vulcanisates against polished ice was measured sequentially at sliding speeds of 10^{-5} ms^{-1} to 1 ms^{-1} in decade steps and at two different temperatures, −4°C and −31°C

TABLE 1 POLYISOPRENE RUBBERS USED

Rubber	Abbrev	Nitrogen level (% mass)	Formulation 1	2	3	4
Synthetic *cis*-polyisoprene[a]	IR	0 01	100	–	–	–
Enzyme deproteinised natural rubber[b]	DPNR	0 08	–	100	–	–
Standard Malaysian Rubber, Grade L	SMR L	0 38	–	–	100	–
Skim natural rubber[b]	Skim	2 19	–	–	–	100
Crosslinking agent[c]			2	2	2	2
Hardness at 21°C (IRHD)			43	40	43	49

[a] *Cariflex IR305* (Shell Chemicals)
[b] Supplied by the Rubber Research Institute of Malaysia
[c] Dicumyl peroxide, *Dicup R* (Hercules)

Each datum point is the average of two friction measurements in reverse directions.

RESULTS

The measured frictional trace *(Figure 2)* showed two types of frictional force, namely starting and kinetic: the starting friction was taken to be the maximum tangential force and may be distinguished from the so-called static friction[4,5]. 'Permanent' static friction has been shown to exist for zero sliding speed when contact surfaces are clean and adhesive, its magnitude depends upon the real area of contact[5]. The static friction is generally less than the starting friction which is rate dependent.

The frictional coefficients, defined as measured friction force divided by applied normal force, corresponding to ice temperatures of −4°C and −31°C and low sliding speeds of 10^{-5} ms^{-1} and 10^{-4} ms^{-1}, are listed in *Table 2*. They reveal that at −4°C, the coefficients for the four rubber types are identical within the limits of experimental error. The results corresponding to cold ice at −31°C however, show that, in general, the friction coefficient increases with the nitrogen content of the rubber. Also the kinetic friction was generally lower than the starting friction.

It is accepted that the area of static contact between a smooth rubber hemisphere and a rigid smooth ice track depends on the hardness (Young's modulus) of the rubber, the contact geometry and the applied load. Classical Hertz theory[6] may be used to calculate the size of the contact area. For the case of an elastic sphere on a rigid planar surface, the contact radius, a, is given by the Hertz equation:

$$a^3 = 9RW/16E$$

where R is the radius of the sphere
W is the normal load on the sphere
E is Young's modulus of the sphere.

From this, the starting frictional stress (force/area) can be calculated. Direct optical observations of the contact interface (where possible) allowed a comparison of calculated and experimental contact areas, and enabled dynamic frictional stresses (force/observed sliding contact area) to be calculated. For opaque vulcanisates (e.g. skim), a Hertz contact area calculation[6] had to suffice. This was fine for the starting frictional stress. For high speed sliding the kinetic frictional stresses of opaque vulcanisates were estimated from the size of any faint wear patches left on the rubber surface after friction testing.

TABLE 2. FRICTION COEFFICIENTS FOR RUBBER TYRES AGAINST POLISHED ICE AT TWO SLIDING SPEEDS

Sliding speed (ms^{-1})	Rubber	Ice temperature −4.0°C ± 0.2°C		Ice temperature −31.0°C ± 0.5°C	
		Starting[a]	Kinetic[a]	Starting[b]	Kinetic[b]
10^{-5}	IR	0.1	0.1	2.9	2.6
	DPNR	0.2	0.1	3.2	3.1
	SMR L	0.1	0.1	3.3	3.1
	SKIM	0.7	0.2	3.8	3.2
10^{-4}	IR	0.1	0.2	3.0	2.8
	DPNR	0.2	0.1	3.6	3.4
	SMR L	0.2	0.2	3.7	3.9
	SKIM	0.5	0.2	4.0	3.4

[a]Uncertainty = 0.05
[b]Uncertainty = 0.1

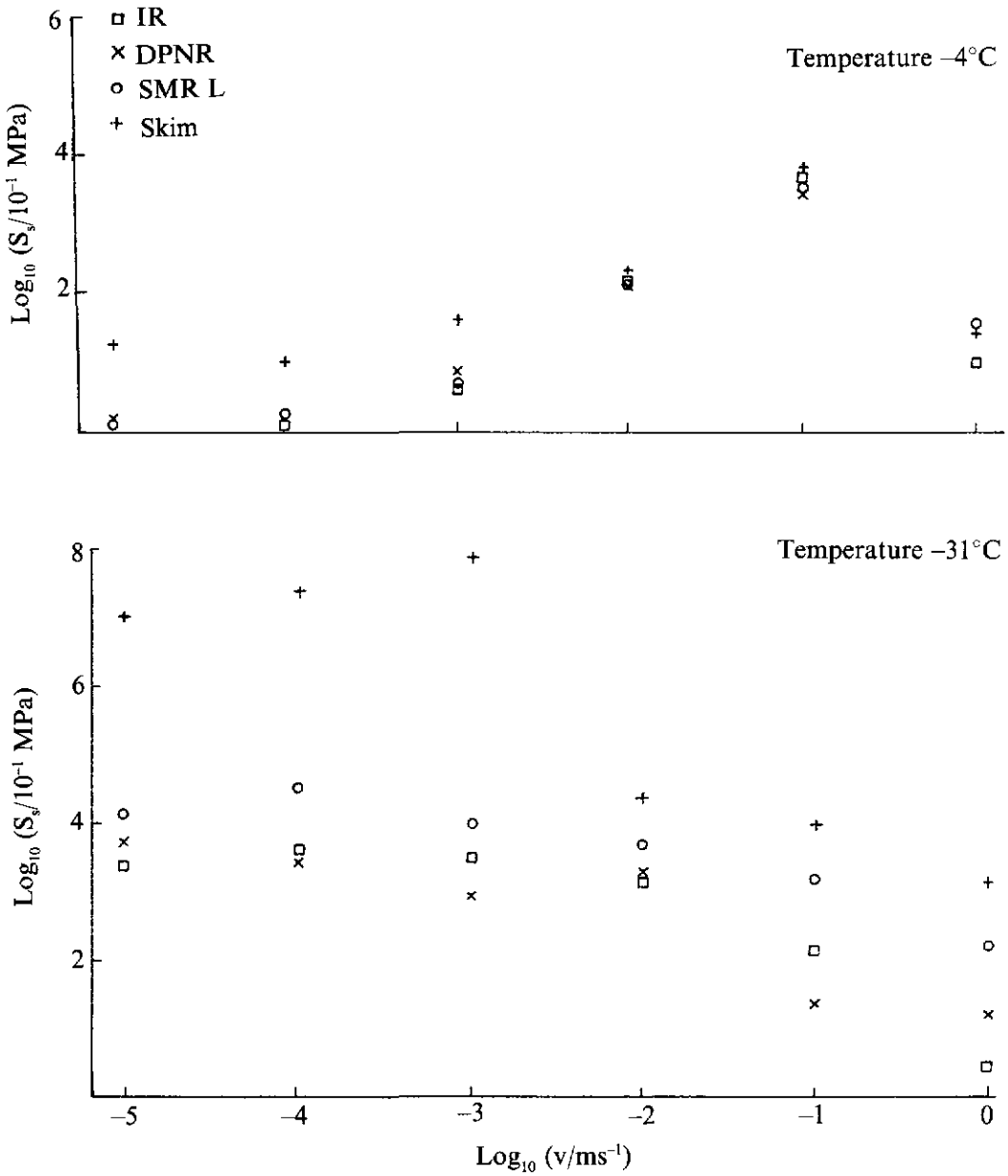

Figure 3. Variation in starting friction stress with speed for four rubber types against polished ice at two temperatures.

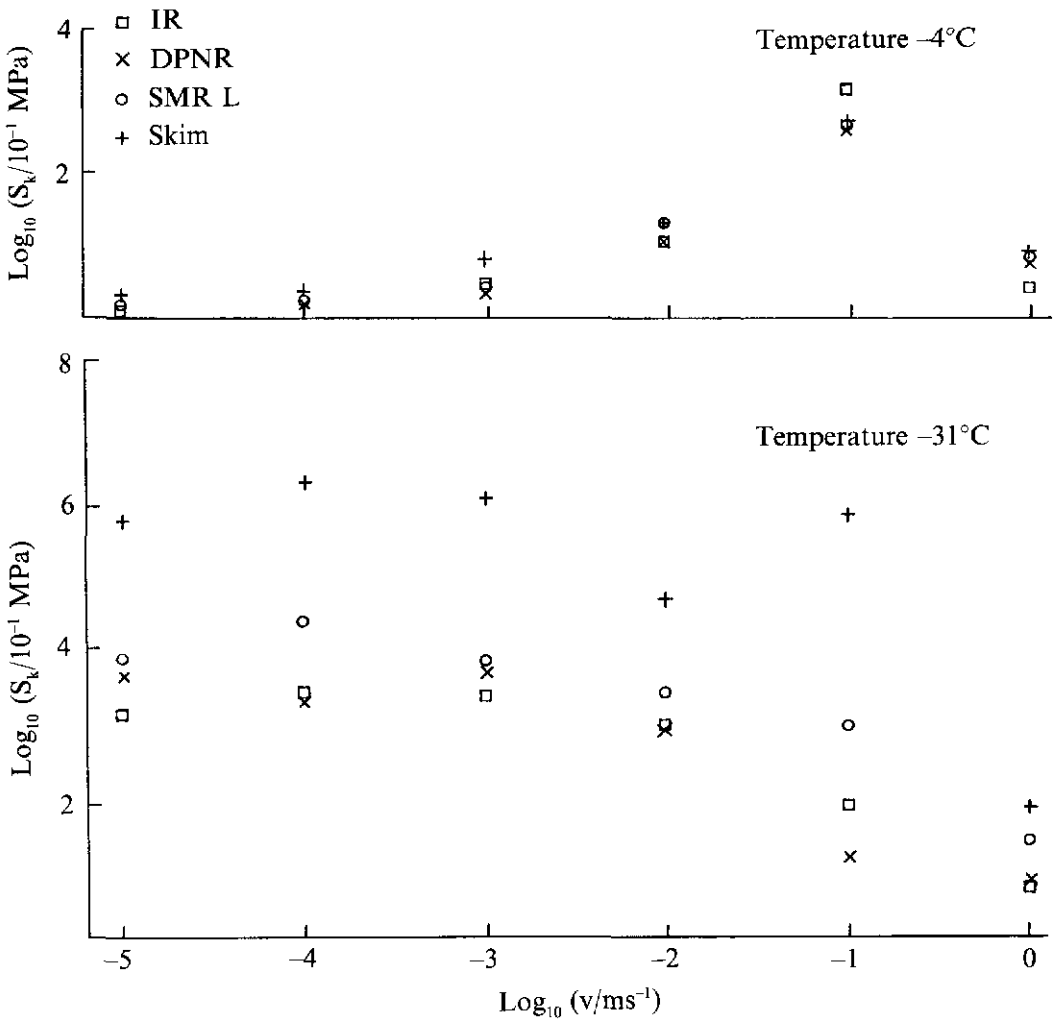

Figure 4. Variation in kinetic friction stress with speed for four rubber types against polished ice.

The calculated frictional stress values at two different temperatures of the various rubbers are shown in *Figures 3* and *4*. For meaningful comparisons to be made between skim and other rubber types, an expected error of 10% based on many observations has been built into the Hertz contact area estimate for skim which, together with the experimental error in the measured friction, is propagated through the analysis to produce final errors in the calculated frictional stress values. At –4°C, this experimental error, for all rubbers, at a speed of 10^{-5} ms^{-1} can be up to 50%, 10^{-4} ms^{-1} up to 25%, 10^{-3} ms^{-1} up to 10% (skim 25%) and at 10^{-2} ms^{-1} to 1 ms^{-1} up to 7% (skim 10%). At –31°C, the error for speeds less than 10^{-2} ms^{-1} is slightly less at 8% (skim 12%).

The starting and kinetic frictional stress data at –4°C (*Figures 3* and *4*) show that up to a sliding speed of 10^{-3} ms^{-1}, the values for

skim rubber are consistently higher than those of IR or DPNR, while above this speed, there is no difference between skim and IR or DPNR data. Optical observations of the dynamic contact interface of IR, DPNR and SMR L rubbers sliding against ice at −4°C indicated the absence of Schallamach waves[2] and no rubber wear up to a speed of 10^{-2} ms^{-1}. At 10^{-1} ms^{-1}, wave fragments[2] and slight rubber wear were visible. At 1 ms^{-1}, bright streaks in the contact interface, indicative of frictional melting of ice, and slight rubber wear but no waves were seen.

Some sequence tests were carried out, for example, the sliding friction of the same SMR L sample was measured in a sequence of rising decade speed intervals from 10^{-5} ms^{-1} to 10^{-2} ms^{-1}. When re-tested at 10^{-5} ms^{-1}, it was found that the frictional coefficients for the two 10^{-5} ms^{-1} measurements coincided within the limits of experimental error. This finding suggests the absence of macroscopic rubber wear, presumably[2,7] due to the presence of surface water and/or flow of the weak ice surface, up to a speed of 10^{-2} ms^{-1}.

On cold ice at −31°C (*Figures 3* and *4*), skim rubber shows higher frictional stress than IR or DPNR. Meaningful comparisons between the rubber types on cold ice is restricted to low sliding speeds, usually less than 10^{-4} ms^{-1}, to avoid complications due to rubber wear and frictional melting of the ice. For all the rubber types, the frictional stress is almost independent of the sliding speed up to 10^{-3} ms^{-1} which is in agreement with previous investigations[2,3].

Optical observations of the dynamic contact interface of IR, DPNR and SMR L rubbers against cold ice at −31°C indicated the presence of Schallamach waves up to a speed of 10^{-3} ms^{-1}. Their presence indicates good grip between rubber and ice: indeed, the sliding frictional stress can be predicted from the observed wave pattern[8]. While SMR L and DPNR showed no detectable wear at 10^{-5} ms^{-1}, they wore rapidly at speeds greater than about 10^{-2} ms^{-1}, reducing the area of real contact, and consequently the friction fell. The extent of rubber wear increased progressively with speed. The synthetic rubber IR showed no detectable wear when slid on cold ice at 10^{-5} ms^{-1} but wear commenced at 10^{-4} ms^{-1} and increased progressively with speed. Visual and microscope examination of the skim rubber surface after a friction measurement showed no detectable wear up to a speed of 10^{-4} ms^{-1}; wear commenced at 10^{-3} ms^{-1}.

Wear patterns produced by sliding against polished ice at 1 ms^{-1} for 10 min are shown in *Figure 5*. It can be seen that wear is particularly pronounced on cold ice. The synthetic rubber IR appears to be weak and shows intense wear. At higher speeds, typically above 10^{-1} ms^{-1}, all rubbers showed some wear at all temperatures, although the extent of wear was much less when sliding on ice near its melting point.

The sliding friction results for all rubber types show that while the friction is high on cold ice, generally below −15°C, it is markedly low on ice near its melting point: this general sharp decline in friction has been noted in previous investigations[2,3,9,10] and is associated with changes in the ice surface properties.

DISCUSSION

One approach to improving the grip of studless tyres on icy or snow-packed roads is to assess the influence of rubber compound on rubber/ice friction. It can be varied in two ways: using rubbers with different molecular structure or by incorporating different chemical ingredients in the rubber. The NR grades used in the present experiments differed in the level of non-rubber material present in the *cis* 1,4-polyisoprene rubber matrix.

Icy road surfaces are inevitably rough and contain various contaminants, in marked contrast to smooth laboratory test surfaces. Nevertheless, tyre trials do show differences in grip according to rubber type[11,12,13], for example, at −27°C, laboratory experiments followed by car rolling and skid

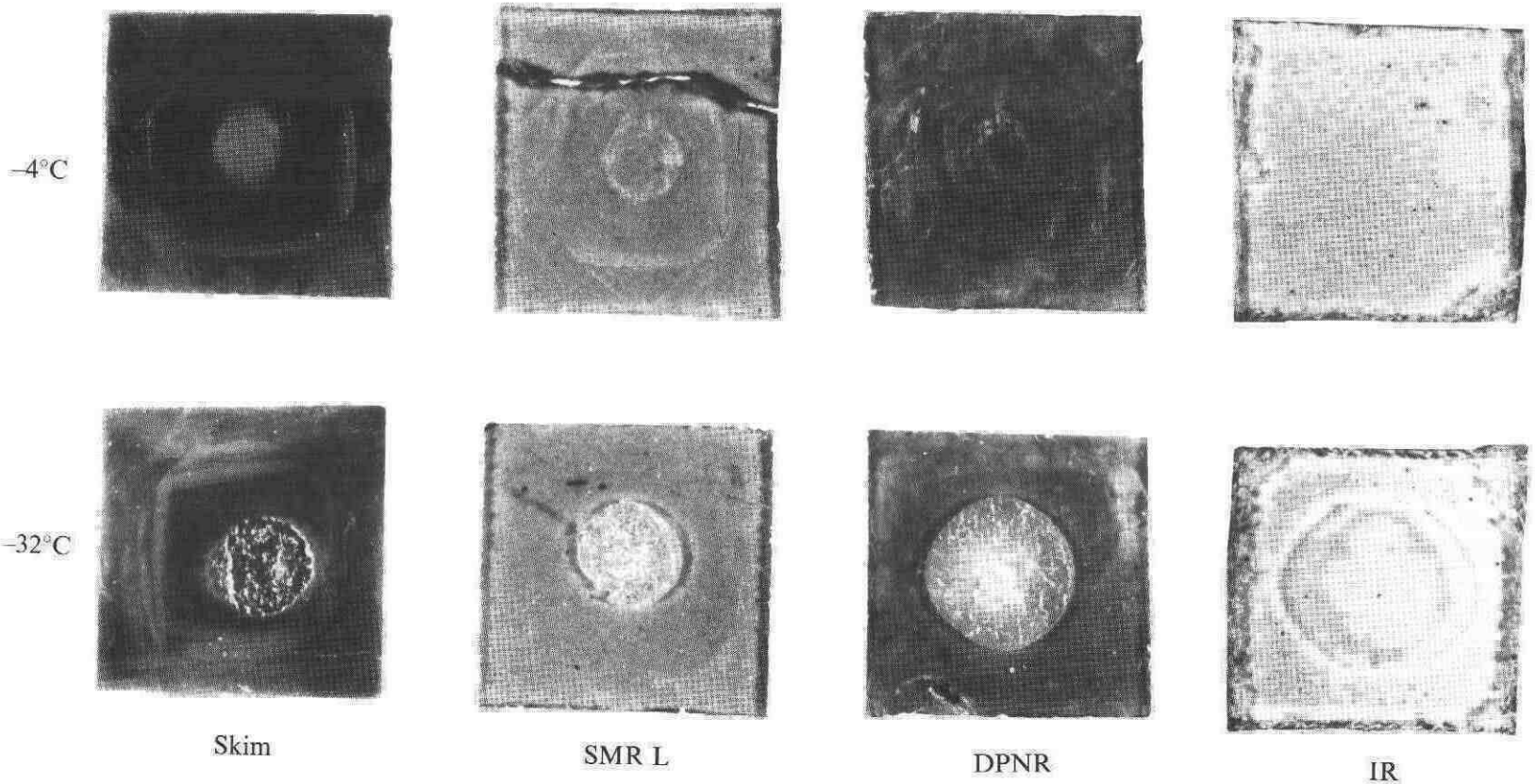

Figure 5. Rubber wear patterns for sliding the four rubbers against polished ice at a speed of 1 ms^{-1} for 10 min at temperatures of –4°C and –32°C.

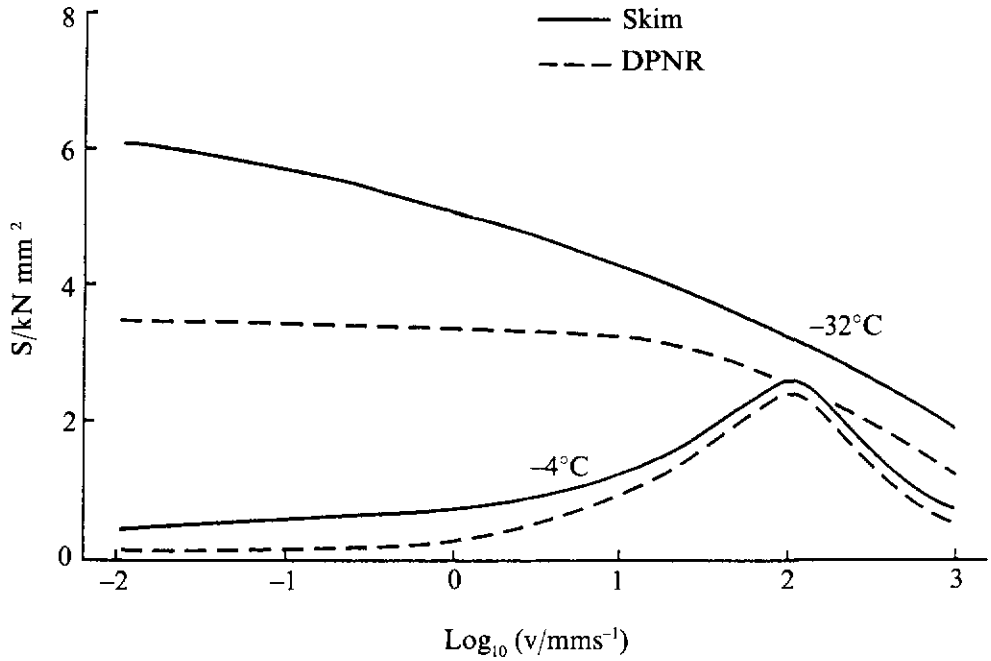

Figure 6. Trends for the sliding shear stress, s, variation with speed, v, and temperature for two types of rubber hemispheres sliding on ice.

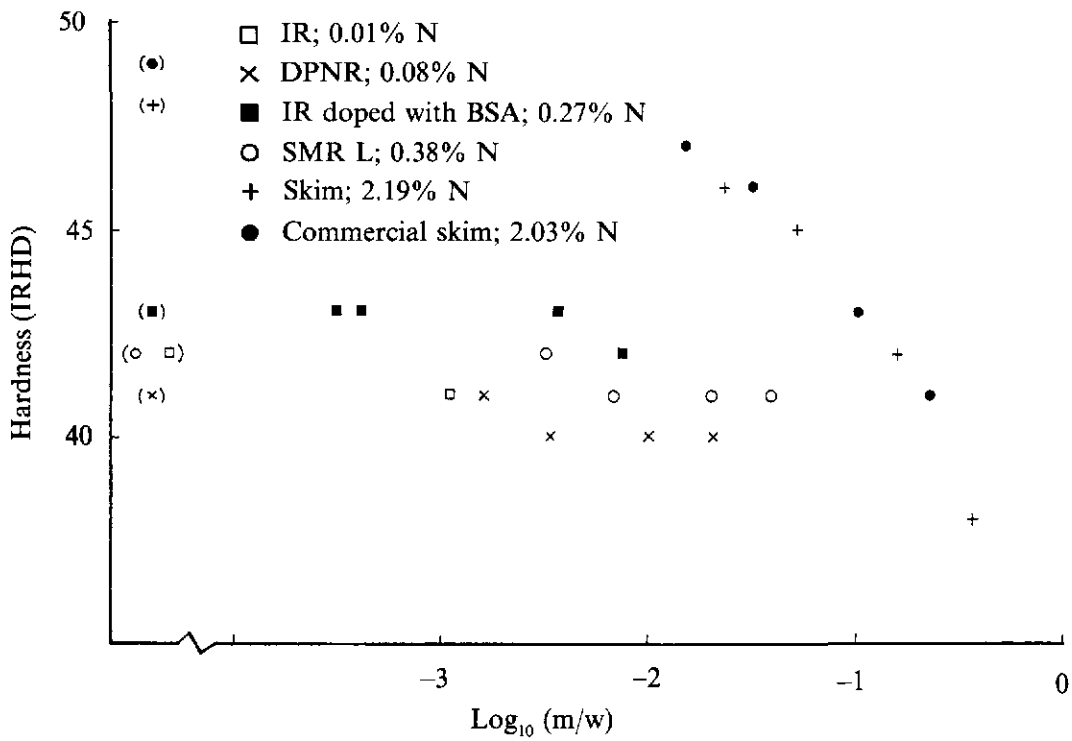

Figure 7. Variation of hardness (International Rubber Hardness Degrees) with water absorbed (log scale) for various gum rubbers (2% dicumyl peroxide-cured) immersed in distilled de-ionised water at 21°C up to fifteen months. The datum points in brackets refer to initial hardness of rubbers (at 50 ± 5% RH) before immersion in water. The water absorbed is measured as the mass uptake, m, per initial mass, w, of rubber sample.

tests[13] have shown a 5% improvement in performance following the partial replacement of carbon black in oil-extended NR treads with silica filler. By comparison, tyre trials at –14°C showed frictional melting of ice which masked the effect of the silica filler on the observed skidding friction. Laboratory experiments on ice near its melting point have shown that the friction is low and generally governed by ice surface properties[2]. Here the importance of tyre tread design as well as rubber type is acknowledged. Even so, at or near to the melting point of ice, some tyre trials do show differences between different tread compounds[11,12].

The present laboratory friction experiments used optically smooth surfaces, ice made from distilled or de-ionised water and gum (unfilled) dicumyl peroxide-cured rubber vulcanisates. Under these ideal conditions, the results on cold ice showed that the sliding friction is influenced by the nitrogen content of the rubber. The comparison is made using trend lines in *Figure 6* for natural rubber of high (skim) and low (DPNR) nitrogen content. The cause of the difference is not known. One can speculate that it relates to the interfacial shear process, or to surface layer softening of the more polar rubbers thereby improving intimate contact.

The effect of water absorption on the hardness of rubbers can be marked; the hardness decreases with increasing water absorption *(Figure 7)*. Skim rubber showed pronounced softening, presumably due to the greater presence of polar groups.

One may speculate on the relevance of these observations to tyre friction on ice. The wheels of a motorcar can display three types of motion: rolling, sliding and contact zone spin. During complex manoeuvres, for example braking during a cornering mode, these motions can occur simultaneously. Normally, however, the wheels exhibit a rolling motion without apparent sliding or spin though there will be some slip at the rear of the contact zone. Treads with high nitrogen content may provide better skid resistance on cold ice but the rolling grip may be reduced[14].

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