

## NEW METHODS OF COMPOUNDING AND THEIR APPLICATION TO THE PROMOTION OF RUBBER IN ENGINEERING

By

J. I. CUNNEEN

(*The Malaysian Rubber Producers' Research Association, Brickendonbury,  
Herts., England.*)

### SUMMARY

*New methods of compounding and vulcanization of natural rubber have led to considerable improvements in the physical properties important in engineering applications. The use of these methods coupled with design, is illustrated by reference to applications such as:*

*bridge bearings; building mountings; anti-impact devices; painted rubber bumpers; engine mountings and pipe sealing rings.*

In Civil Automotive and Mechanical Engineering, the competition for natural rubber (NR) is as much with steel as with synthetic rubber (SR). The engineer in the past has always considered steel and concrete as his basic materials and has not been inclined to use rubber. The properties which have mainly imposed limitations on the use of rubber as compared to steel are: lack of design—performance information, less precision in manufacture and excessive creep (this is the slow deformation which takes place under load over long periods of time). The factors influencing these properties have been investigated at the MRPRA and substantial improvements have been made in two ways: (i) by varying the properties of the material *via* a new form of NR and a new method of compounding; and (ii) by correct design of components. The new method of vulcanization is orthodox in that it uses sulphur and well known accelerators but in different combinations from those used hitherto, whereas a second method which will be described in the next paper is unorthodox since no sulphur compounds are used.

### *Soluble Vulcanizing Systems*

This method of vulcanization has been developed by Dr. J. F. Smith at MRPRA and it arose in the following way. All rubbers show a decrease in strength as the temperature of testing is raised, and this decrease usually becomes catastrophically rapid around a characteristic temperature (which incidentally is higher for NR than SR). The general scatter of results in strength testing grows larger as the test temperature is increased so that, in practice, results fall within a quite wide band around the characteristic temperature (Fig. 1). It was found that this scatter is due to inhomogeneous vulcanization caused by maldispersion of curatives existing in mixes made on the conventional rubber mill. This was demonstrated by compounding the same formulation but adding finely ground dispersions of the curatives to NR latex and then coagulating, drying, and lightly milling the dry coagulum at 40°C, a procedure described in the paper by Dr. Cockbain. The strength results on the vulcanizates now fell into a narrow band at the high-temperature end of the previously observed band (Elliott *et al.*, 1969) (Fig. 1). Microscopic examination of the mixes prepared in the two different ways showed that there are two sources of maldispersion of curatives: (i) loose aggregation of fine powders, and (ii) a time-dependent crystal-coarsening process which takes place after mixing. The second process is particularly noticeable with sulphur.

These observations have led to the concept of soluble compounding, that is, the formulation of a rubber mix in such a way that all the ingredients (with the exception of zinc oxide and any insoluble filler which does not re-aggregate on storage) remain soluble in the rubber at ambient temperature (Smith, 1973). It is not easy to formulate vulcanizing systems in this way since the solubility of sulphur in rubber at 20°C is only about 0.8%, but this has been achieved with EV systems where the sulphur concentration is below this level (Table 1). Although the improvements conferred by soluble compounding were considerable, some unwanted variability was found on prolonged storage. This was traced to the effect of water absorption, which changes the cure characteristics and hence properties such as modulus. Removal of natural hydrophilic impurities by enzymic deproteinization of latex was investigated and found feasible (Smith, 1973) and enzyme deproteinized NR (DPNR) is now being produced in tonnage quantities by the Rubber Research Institute of Malaysia. Typical analytical figures obtained are given in Table 2. The principal advantages of soluble EV systems and DPNR over normal EV, conventional systems and normal NR are that they provide vulcanizates which: are highly reproducible with respect to stiffness (Table 3); show improved creep (Table 4); improved resilience and lower heat build-up (Fig. 2); reduced compression set and reduced rate of stress relaxation (Table 5). These properties as will be apparent later are very important in engineering. The influence of the two factors mentioned above and of design, on the use of rubber in engineering is illustrated by reference to some of the prominent examples of engineering applications.

#### *Bridge Bearings*

These bearings are mounted between the bridge deck and the supporting piers. The load-deflection characteristics required of the bearing are that it should resist vertical movements, but be able to take up horizontal movement due to expansion of the bridge deck. These characteristics have been achieved by a design based on MRPRA research which incorporates horizontal metal plates, as shown (Anon) (Fig. 3). Low temperature characteristics, longevity, low set and creep are also important and NR suitably compounded is excellent in these respects. This is an application which uses high quality NR (RSS1, SMR5) and virtually all medium-span bridges built in Britain today (≈ 500 per year using 0.5 tons of rubber per bridge) are mounted on NR bearings, instead of metal roller bearings. Canada, New Zealand and Australia also largely favour NR. Future work in this area is mainly concerned with promotion *i.e.* persuading other parts of the world to use NR bridge bearings. Some success has already been achieved for example, the USA specification for bridge bearings now includes NR whereas previously it was limited to polychloroprene (CR) and in February this year the Gumakov factory in Czechoslovakia has started the production of NR bridge bearings. This latter was initiated by lectures given in Czechoslovakia by members of the MRPRA Engineering Section. In Germany and Italy, CR is still favoured rather than NR, although it suffers from two disadvantages—it crystallizes more rapidly than NR at low temperatures and it is more costly. NR's excellence for this application is fully proven by the example of the Pelham Bridge at Lincoln in the UK (Fig. 4). This was the first major bridge fitted with laminated NR steel bearings some 17 years ago when inspected in March last year the NR bearings were found to be in perfect condition.

#### *Building Mountings*

Rubber mountings have been used for some years as a means of isolating buildings from the effects of ground-borne vibration due to, for example, nearby surface or underground railways (Crockett, 1973). The most important property in this application is creep, which must be kept to a minimum. The creep of a 1400 ton building on NR mountings has been monitored (Fig. 5) for seven years. So far it

has exactly followed the predictions of short term laboratory experiments, and the expected life of the buildings before it will settle on the foundations is >100 years. Very low creep rates of this sort can easily be achieved with the new NR compounds referred to above. Although building mountings are so far used only to a limited extent, world wide interest is growing and there is substantial interest in Eastern Europe (the Gumakov factory has started development work), Australia and the USA. A working party containing two members of the MRPA, one of whom is the chairman, has produced a document which has been submitted to the British Standards Institution in order to introduce a specification for rubber building mounts in the UK. (As with bridge bearings other countries are likely to adopt wholly or in part the UK recommendations).

At the present time an extension of this application and what constitutes a new use for NR is being pursued in collaboration with Atkins Research and Development Co. This is the possible use of NR mountings to isolate buildings from shock due to earthquakes, here creep resistance will be particularly important. The significance of this application to certain parts of the world is obvious.

#### *Anti-Impact Devices*

NR has traditionally been used in impact absorbing devices particularly in packaging, bumper stops and dock fenders (Allen *et al.*, 1967). When legislation was introduced in the USA recently (US Federal regulations for 1973 cars) requiring that cars must sustain no damage to safety-related components on impact into a stationary rigid object at 5 mph, it was realized that this could be achieved using NR as the energy absorbing material. A preliminary design using rubber in shear was published by Lindley in 1970 (Fig. 6), and copies were circulated to car manufacturers worldwide. Considerable interest was shown by Ford (Detroit), discussions with MRPA took place, and Ford announced that all but their smallest 1973 and 1974 models will have an energy absorber (FEA) based on NR (Slessor *et al.*, 1973). This is expected to consume 4000 tons of NR per annum and could grow considerably if similar devices are used by other manufacturers.

This year an ISO standard has been proposed for impact absorbers (2½ mph), and there is a strong possibility of it being taken up by European and UK Government bodies. A low speed requirement such as this will almost certainly be met by a rubber device (may be a whole rubber bumper), rather than hydraulic, but competition is developing from polyurethane, polyisobutylene (butyl) and ethylenepropylene (EPDM) rubber. Comparative studies are being carried out in the laboratory and present indications are, that NR may have advantages over polyurethane and butyl since their stiffness probably varies too much over the operative temperature range (-20° to +50° C). A further condition attached to the development of rubber bumpers is that they should be decoratively finished with a glossy paint matching the colour of the car. Photochemical and chemical treatments have been developed which improve paint adhesion, (Cutts *et al.*) and bumpers have been made by injection moulding techniques from NR and soluble recipes which have an excellent appearance coupled with good abrasion and weathering resistance. This painting technique will, of course, be useful for other visible rubber components on cars.

#### *Engine Mountings*

Automotive engine mounts have traditionally been made of NR (annual consumption 5-10,000 tons), and in general they have performed well. Recently the installation of antipollution devices in American cars has led to increases in underbonnet temperatures, some predictions giving values as high as 180°C.

Visits have been made recently to car manufacturers in the UK and the USA and their tests have indicated that using anti-pollution devices in the presence of insulation, the temperatures attained by engine mounts were  $<120^{\circ}\text{C}$ . In the absence of insulation very high temperatures (no figures available) were reached and numerous problems with other components were also encountered.

At the present time the performance of NR compounds is being investigated in the range  $100\text{--}150^{\circ}\text{C}$ , in order to find out the capabilities of current compounds and what improvements can be effected. The engine mounts used in several models of cars from the UK, Europe, Japan and the USA have been analysed. Seventeen of the nineteen samples were NR and the majority were conventionally cured. The strength properties of thin and thick samples of conventional, semi-EV, soluble EV and peroxide vulcanizates are being investigated after ageing at temperatures up to  $150^{\circ}\text{C}$  in air, and under anaerobic conditions. The thick samples more closely resemble engine mounts which have a relatively small surface to volume ratio; at  $100\text{--}150^{\circ}\text{C}$  oxidative degradation is confined to a thin surface layer, the bulk of the material ageing anaerobically. In general, the surface first softens and subsequently hardens to a brittle skin on ageing. The hard skin is deleterious to fatigue strength, as it ruptures at low elongation and produces cracks, which propagate into the relatively sound material below. As expected the soluble EV and peroxide vulcanizates show improvements over the conventional compound. Investigations involving the addition of some novel reagents are also being carried out, to see whether further improvements can be obtained.

### *Pipe Sealing Rings*

Movements of the earth will cause rigid pipelines to break if the sections of the pipe are not provided with flexible joints (Clarke *et al.*, 1967). Rubber O-rings (annual consumption 20-30,000 tons) have been used for many years in these joints to accommodate axial and bending movements of the pipeline (Fig.7). Having been introduced to provide flexibility the rings must also prevent leakage, and in this respect their effectiveness depends on the maintenance for a very long time ( $>50$  years) (Table 5) of a sealing stress sufficient to resist the fluid pressure. Correct design and installation will ensure that sealing is initially effective, but allowance must be made for the inevitable loss with time, of stress in the seal (Derham & Lindley, 1971). Stress relaxation, therefore, is the property most dominant in determining long term performance, and it should be measured on all compounds to be used in pipe sealing applications. Furthermore, such measurements should be made with the rubber in contact with the fluid to be carried in the pipeline, since it has been shown that the presence of water can affect the stress relaxation rate of a number of polymers (Derham, 1972). Fig. 8 shows that polychloroprene, NR's chief competitor in this application is much worse than NR in the presence of water, and that soluble compounding with DPNR leads to improvements. Resistance of sealing rings to microbiological attack is also another factor which has received much publicity in recent years. (Leefflang, 1963; Dickenson, 1969). However, this can now be effectively retarded by suitable compounding, (Cunneen & Dickenson) and furthermore synthetic rubber is also attacked (Anon, 1970).

TABLE 1  
TYPICAL SOLUBLE EV RECIPE

Rubber	100
Zinc Oxide (ZnO)	5
Zinc 2-ethylhexanate (ZEH)	2
Sulphur (S)	0.4-0.8
Tetrabutylthiuram Disulphide (TBTD)	0.4-0.8
2-Morpholinothio-benzothiazole (MOR)	0.96-1.92
Diphenylguanidine (DPG) (boost)	0.6 (if required)

TABLE 2  
ANALYSIS OF DPNR (PILOT PRODUCTION VALUES)

	Dirt %	Ash %	Nitrogen %	Free fatty acid % expressed as stearic acid	Acetone extract %	Colour Lovibond Units	Mooney Viscosity 100°C
Mean	0.006	0.026	0.056	1.42	3.22	6.2	63.8
Standard deviation	0.001	0.010	0.007	0.10	0.26	0.8	1.6

TABLE 3  
PRECISION OF SPRING STIFFNESS

Cure System	Rubber	Modulus Variability*
Conventional sulphur	RSS 1	±13%
Soluble EV	RSS 1	±4%
Soluble EV	DPNR	±2%

\* 95% Confidence Limits

TABLE 4  
CREEP RATE AT 28°C

Type of Compound	Creep Rate	Time to increase deformation at 1 day by 2%
Conventional/RSS1	2% per decade	10 days
Soluble EV/RSS1	1% „ „	100 days
Soluble EV/DPNR	0.4% „ „	> 100 years

TABLE 5  
SEALING RING COMPOUNDS

Type of Compound	Time to lose 25% of initial stress
Conventional/RSS1	10 weeks
Soluble EV/RSS 1	20 years
Soluble EV/DPNR	200 years

# 95% CONFIDENCE LIMITS IN STRENGTH TESTING OF VULCANIZATES

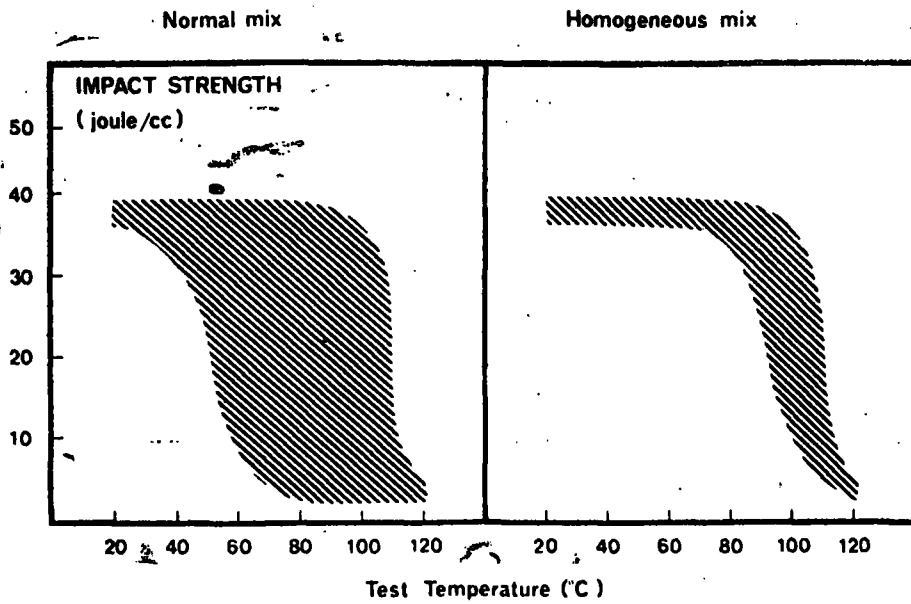


Fig. 1 95% Confidence Limits in Strength Testing of Vulcanizates

Figure 2

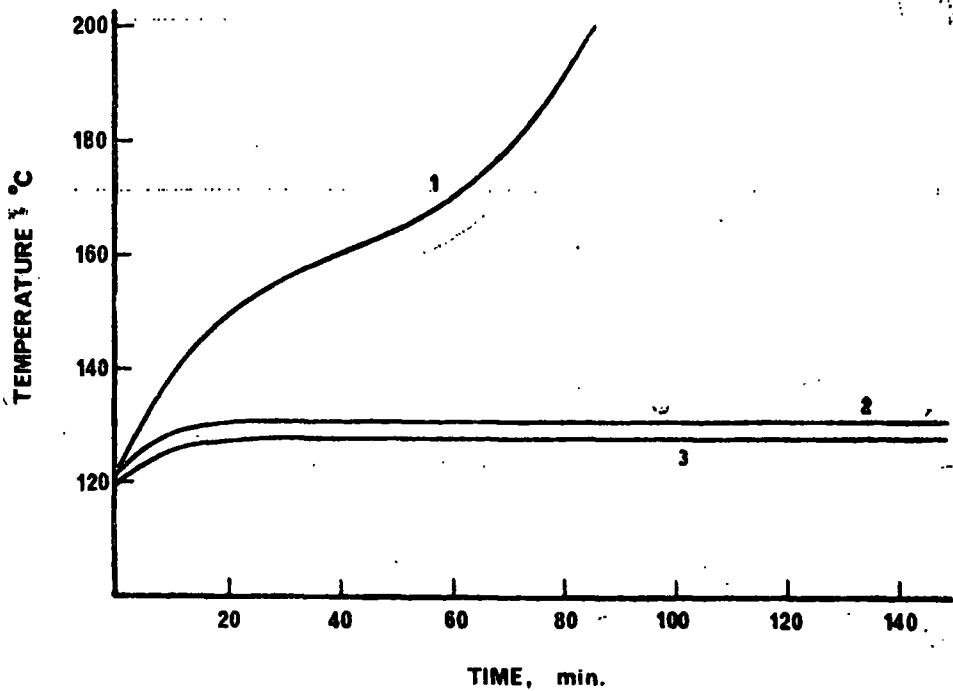


Fig. 2 Heat Build-up of NR Vulcanizates, Goodrich Flexometer Test

- (1) RSSI, CBS accelerated sulphur
- (2) RSSI, soluble EV
- (3) Deproteinized NR, soluble EV

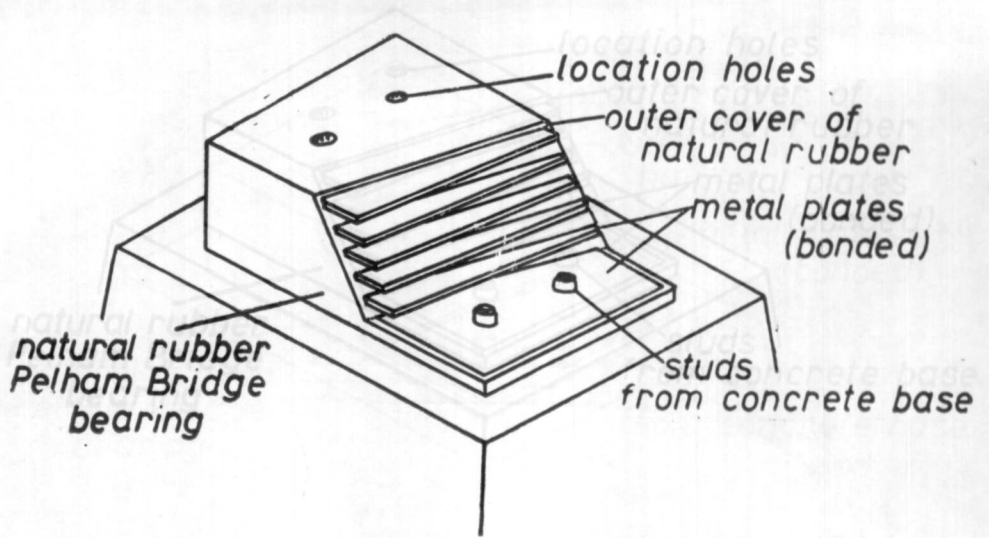


Fig. 3 Laminated NR/Steel Bridge Bearing

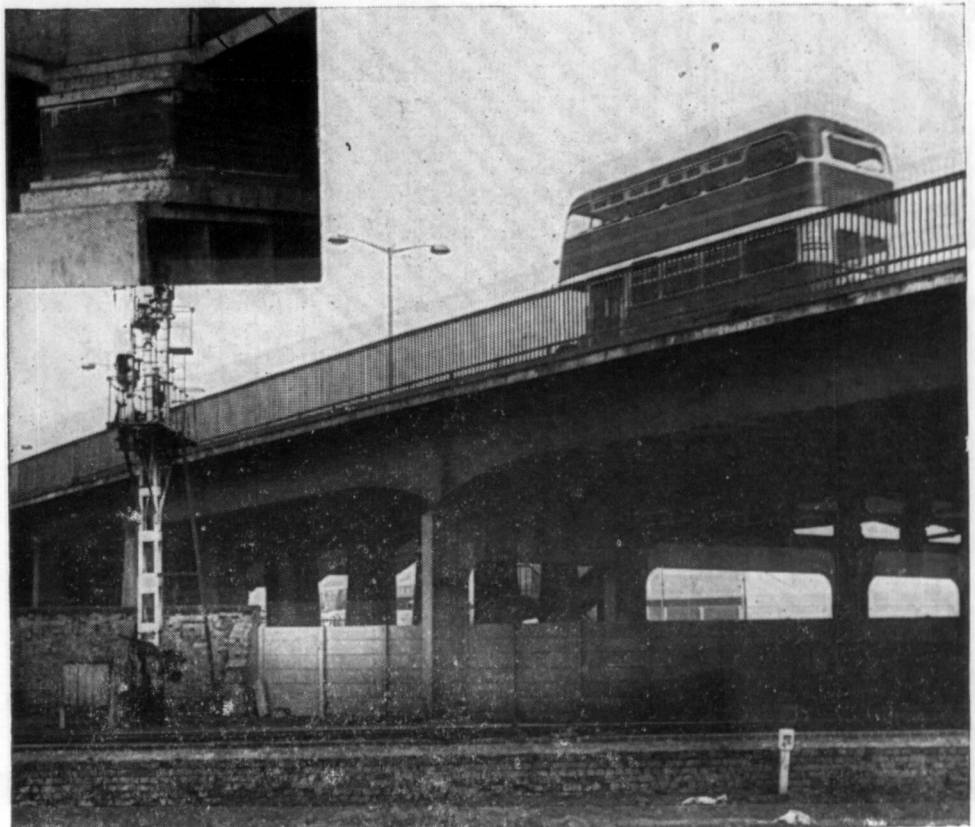


Fig. 4 NR Bearings Supporting the Pelham Bridge, Lincoln, England

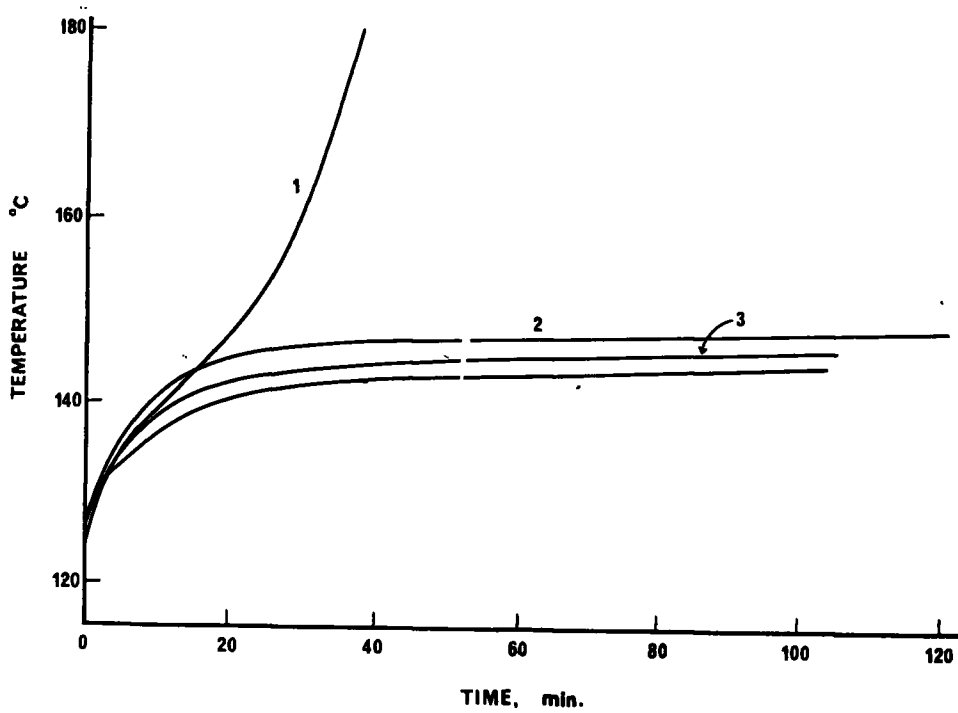


Fig. 5 Heat Build-up of NR Vulcanizates, Goodrich Flexometer Test

- (1) RSSI, CBS accelerated sulphur
- (2) RSSI, urethane
- (3) RSSI, Soluble EV
- (4) Deproteinized NR, soluble EV

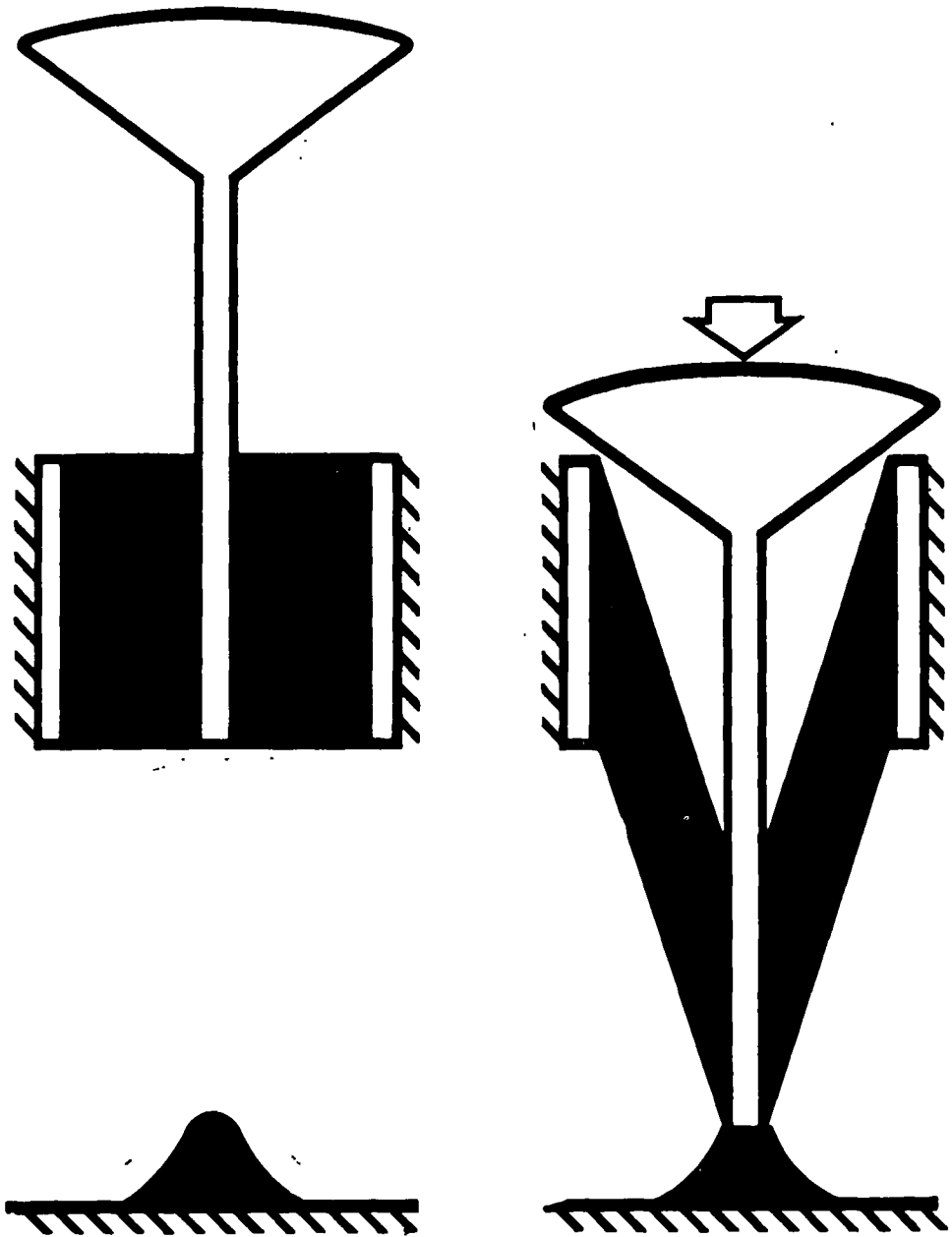


Fig. 6 N.R.P.R.A Design of Anti-impact Device Using NR in shear

10/15

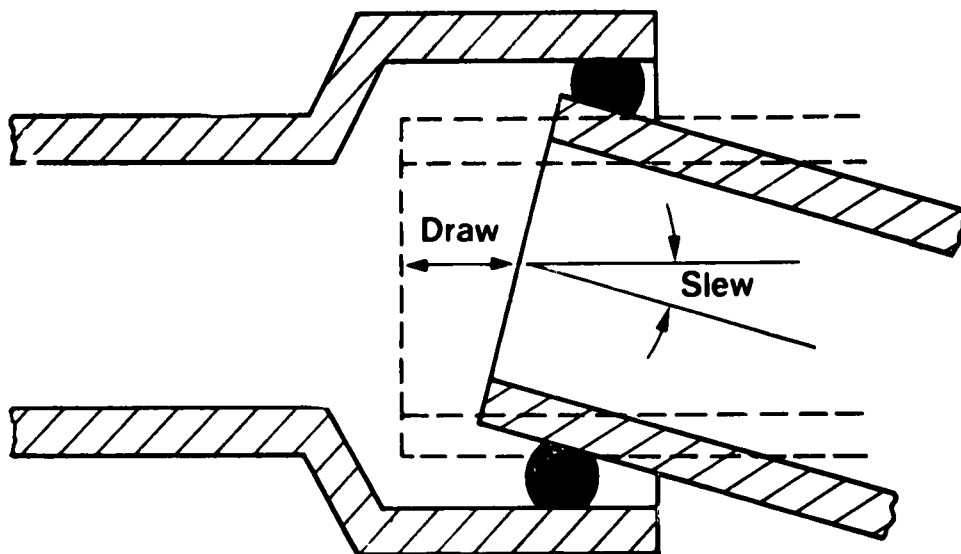


Fig. 7 Rubber O-ring Providing a Flexible Joint

Figure 8

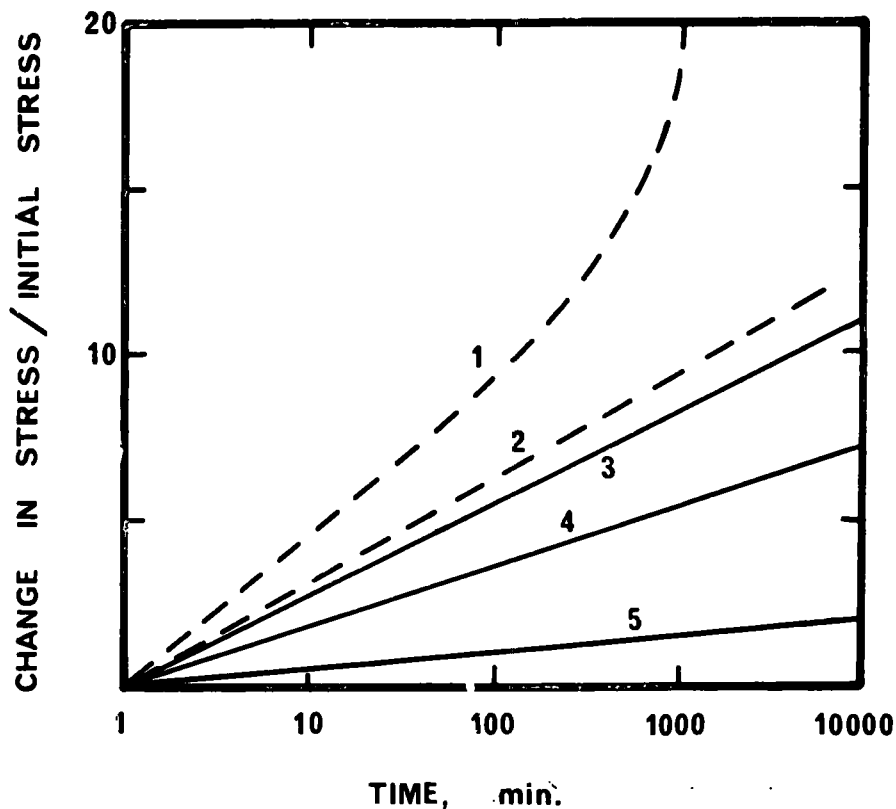


Fig. 8 Stress Relaxation of Vulcanizate in Dry (36% humidity) and Wet (88% humidity) Environments

- (1) Polychloroprene (Neoprene WRT) cured with a typical zinc oxide, magnesium oxide recipe, wet
- (2) As for (1), dry
- (3) SMR5, CBS accelerated sulphur, wet
- (4) As for (3), dry
- (5) Deproteinized NR, soluble EV, dry

REFERENCES

- ALLEN, D. C. (1967). *Use of Rubber in Engineering*. ed. P. W. ALLEN, *et al.*, ch. 17, London: Maclaren & Sons Ltd.
- ANON. *Tech. Bull. Natu. Rubb. Prod. Res. Ass.* No. 7, London: NRPRRA.
- ANON. (1970). Natural Rubber Producers' Research Association. Annual Report for 1969, p. 36.
- CLARKE, N. W. B. (1967). *Use of Rubber in Engineering*. ed. P. W. ALLEN *et al.*, ch. 10. London: Maclaren & Sons Ltd.
- CROCKETT, J. H. A. (1973). Recent developments in spring insulated buildings. In *Rubber in Engineering 1973*. ed. P. B. LINDLEY and H. G. RODWAY, pp. B1-B9. London. NRPRRA.
- CUNNEEN, J. I. AND DICKENSON, P. B. *British Patent Application No. 36519/71*
- CUTTS, E., KNIGHT, G. AND WHEELANS, M. A. Unpublished work.
- DERHAM, C. J. (1972). *Proc. International Rubber Conference, Brighton 1972*.
- DERHAM, C. J. AND LINDLEY, P. B. (1971). *Proc. 5th International Conference on Fluid Sealing, Warwick, 1971*.
- DICKENSON, P. B. (1969). Natural Rubber and its Traditional use in underground pipe sealing rings. *J. Rubb. Res. Inst. Malaya*. 22 (2), 165-175.
- ELLIOTT, D. J., SKINNER, T. D. AND SMITH, J. F. (1970). Compounding of natural rubber for engineering applications. *NR Technology 1970*. Part 3 No. 13. pp. 2-17. Paper read at *International Rubber conference, Moscow 1969*:
- LEEFLANG, K. W. H. (1963). *J. Am. Wat. Wks. Ass.* 55 (12), 1523.
- LINDLEY, P. B. (1970). *Automotive Engineering* 78 (12), 30.
- SLESSOR, J. M., RUSCH, K. C. AND PETT, R. A. (1973). *Proc. International Automotive Engineering Congress, in Debroit, U.S.A.*
- SMITH, J. F. (1973). Natural rubber compounds for low creep and improved dynamic performance. In *Rubber in Engineering 1973*, ed. P. B. LINDLEY & H. G. RODWAY, pp. G1-G9, London: NRPRRA.