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Natural Rubber and its Traditional Use in Underground Pipe Sealing Rings

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Natural rubber is acknowledged as the best elastomer for use in pipe sealing rings in underground situations but recently it has been suggested that rare cases of corrosion are caused by direct micro-biological attack on the natural rubber component. This diagnosis is critically examined in the light of modern knowledge and current research, and the nature and the extent of corrosion is considered in relation to the known satisfactory performance of many millions of natural rubber pipe sealing rings over the last hundred years.

Because of its outstanding properties in terms of resilience, tensile strength, resistance to compression set and resistance to certain types of effluent, vulcanised natural rubber when suitably compounded has long been acknowledged as the supreme elastomer for use in pipe sealing rings in underground situations. Indeed, many millions of such rings have been used over the last hundred years or more and occasional excavations have revealed remarkable cases of longevity in rings buried for this period yet still retaining eminently serviceable characteristics (DUNKLEY, 1964).

Recently however, there have been occasional reports, notably from very localised areas in Holland, Australia, New Zealand and America of superficial or deeper surface corrosion of vulcanised natural rubber sealing rings used in water main or sewerage pipelines. This, it is pertinent to state, has invariably been observed on rings retrieved during excavations concerned with pipeline alterations, or building operations and not detected as a direct consequence of the failure of a joint leading to an exploratory excavation. Indeed, cases of actual failure are so few as to be trivial when compared with the astronomically large numbers of rings in use, and defects caused by improper compounding resulting in, for example, excessive compression set, are of much greater consequence, as indeed are the failures caused by the improper use of satisfactory rings or by the use of rings compounded from inferior rubbers. The extent and the effect of this corrosion when seen in perspective may be compared, not inappropriately, with the rusting of unprotected steel—equally a nuisance but also one which does not detract from the supreme excellence of the material for the purpose concerned.

In areas of Holland, where corrosion has been most pronounced, there have been five or six actual failures in cement-asbestos water main pipelines and some in America in a pressurised water main, but where the prime cause of failure, in rings examined by the N.R.P.R.A., appeared to be a pronounced degree of compression set. From the Antipodes, and Australia, in particular, searching enquiries have shown that, although corrosion has been observed, no actual mechanical failures have occurred except for a very few isolated cases in sewerage pipe joints caused by plant root penetration. Nevertheless, a degree of alarm exists over the apparent susceptibility to corrosion of natural rubber vulcanisate and this, in certain countries, has been sufficient to lower confidence in the long term performance of the polymer to the extent that at the extreme—as in certain regions of Australia—any case of reported corrosion is regarded as a 'failure'.

LEEFLANG (1963) concluded from his own examination of the local phenomenon in Holland, that the primary cause of this type of

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corrosion was the presence of common soil-borne micro-organisms belonging to the genus *Streptomyces*, which he regarded as able to utilise vulcanised natural rubber hydrocarbon as a carbon source. In the absence of reassuring evidence to the contrary, it is perhaps understandable that users of natural rubber for this purpose should have felt alarm at the suggestion of an inherent 'defect' with its implication of the possibility of more widespread, if unseen, underground deterioration. Indeed, such has been the hasty and irrational condemnation of natural rubber for use underground in moist situations, that at least one national standards specification has been amended in favour of inferior synthetic rubber substitutes and this in a country where corrosion, let alone failure, of natural rubber pipe sealing rings has never been observed.

LEEFLANG (1963) whose careful researches followed those of ROOK (1955), demonstrated by isolation on to suitable non-selective culture media the presence in superficially corroded Dutch water main natural rubber pipe sealing rings of large populations of *Streptomyces* spp. Such corrosion was confined to limited areas of Holland served by 'dune water' supplies of an unusual nature, unchlorinated and of relatively high phosphate content, and it was most obvious in the Simplex joints of cement asbestos water main pipes where a sleeve of the same material confines a pair of sealing rings to the surface of the pipe. In this special type of joint, a large part of the surface of the ring is exposed to the transported water in the dead-space of the sleeve interior, and to the ground water outside. Corrosion was most noticeable on the transported water side of the rings. In screw type joints, with much less rubber exposed to the water, corrosion was barely detectable. When, in other countries such as Australia, corrosion has been found in NR sewerage pipe jointing rings, it has usually been limited to the region in the air space above the liquid level, the general nature of sewage being anaerobic, and the requirements of *Streptomyces* aerobic.

ROOK (1955) had deduced that, under laboratory conditions, pure cultures of certain strains of *Streptomyces* isolated from such rings, would apparently attack thin strips of vulcanised natural rubber and this appeared to confirm the early claims of SÖHNGEN AND FOL (1914) and SPENCE AND VAN NIEL (1936), among others, that natural rubber may be consumed by micro-organisms of this type. Such a view at first sight may seem reasonable, since there exists abundant evidence that various micro-organisms possess the ability to utilise unusual carbon sources, including hydrocarbons, for growth.

The findings of LEEFLANG (1963) were based upon a simulated field test in which, under laboratory conditions, a number of rings of natural or synthetic rubbers, from commercial sources, or compounded from formulations of an experimental nature, were tested for their resistance to corrosion. They were immersed in test tanks through which a slow flow of the local mains water was maintained after first passing over an 'inoculum' consisting of a portion of a corroded natural rubber ring known to contain *Streptomyces* in quantity.

The results of this test seemed to indicate, that with the notable exception of a natural rubber ring of Swiss manufacture, all natural rubber compounds and synthetic *cis*-polyisoprene compounds tested were susceptible to corrosion, sometimes showing signs of it as early as two to three months, while all the other synthetic rubbers were immune over a period of at least two years. Mixtures of natural with synthetic rubber showed a similar immunity provided that the proportion of natural rubber did not exceed 40–50%. Assessment of degrees of attack was tactile, for, with the apparent loss of rubber hydrocarbon from the corroded surface, the filler material is left, and when this is predominantly carbon black, a sensitive although qualitative estimation of the onset and degree of corrosion may be made.

This simulated field test has been duplicated at the N.R.P.R.A. laboratories, but with the important difference that, in the absence of indigenous species of *Streptomyces* associated with NR vulcanisate corrosion, strains obtained from other countries, namely Holland and Australia have had to be used as the inocula. Here, too, very slow corrosion has been induced experimentally in certain test specimens, thus demonstrating circumstantial association of it with *Streptomyces* transferred to a strange environment, the principal differences being that in the Dutch test area, the local water is unchlorinated and of relatively high phosphate content, while under the English conditions, residual chlorine is present to the extent of 0.4 p.p.m. maximum, while the phosphate content is less by a factor of five. HILLS (1967) has also conducted a similar test in New Zealand, where superficial corrosion of NR sewerage rings has been observed.

Pending the results of continuing investigations of a complex phenomenon, a reasonable conclusion as a basis for working hypotheses was of a causal relationship between the presence of *Streptomyces* and surface corrosion under some service or test conditions, of some but, as LEEFLANG (1963) demonstrated, not all natural rubber vulcanisates.

It has been pointed out however, by DICKENSON (1965a) that a survey of the relevant literature of the past fifty years reveals no *unequivocal* evidence for the direct utilisation as a carbon source of natural rubber hydrocarbon, vulcanised or not, by micro-organisms, and that simulated field tests, although indicating a circumstantial association of one group of them with a very complex mixture of materials, equally do not provide it. Further, the conclusion of LEEFLANG (1963) that synthetic rubbers were 'immune' to attack under these test conditions was regarded as invalid, since the tests had an inherent and inescapable bias in favour of the 'immunity' of synthetic rubbers because of their exposure only to inocula obtained from corroded vulcanised NR. The molecular configuration of synthetic rubbers is dissimilar enough from that of natural rubber to preclude their utilisation by the test organism, which, *if* consuming natural rubber in *any* form, must, by mutation and/or adaptation with subsequent selection, have acquired the ability to do so. Implicit in this ability is the possession of the necessary specific enzyme system capable of catalysing the oxidation of the substrate to carbon dioxide.

The present paper describes preliminary researches into this very complex problem in which its prevalence has been investigated and the published diagnosis of its cause critically examined in the light of modern knowledge. Experimental work, which is in progress, has been based upon the need to ensure full protection for natural rubber products under any adverse service conditions and to achieve this end speedily and rationally, rather than empirically, further consideration has been given to the specific role played by the circumstantially associated micro-organisms.

EXAMINATION OF SPECIMENS

Investigations have been limited because of a scarcity of material for examination, but a few specimens have been received from Holland, Australia, New Zealand and Sweden through the agency of collaborating workers, or from locally based M.R.F.B. Technical Advisory Service staff. Only one corroded specimen for examination has been received from overseas following a widely circulated published invitation stating that these laboratories would welcome such material (DICKENSON, 1965b). It may be that the absence of response is more an indication of the extreme rarity of the phenomenon rather than of any lack of interest in it.

Chemical Analyses

Three specimens of slightly corroded water main pipe sealing rings of Dutch origin, one of them having been in service for twenty-three years, were chemically analysed. It was found that although one showed a substantial degree of compression set, all were admirably compounded to a very good quality formulation with an adequate natural rubber content. All would clearly have had a substantial number of years of satisfactory service life ahead of them at the time of examination.

From these analyses, however, it appeared at first that there was no significant amount of anti-oxidant present, but subsequent investigation using refined techniques of thin-layer chromatography possessing high sensitivity showed the presence, at very low level, of an anti-oxidant of the phenyl-β-naphthylamine (PBN) type. Approximate values were, in one ring, 0.3 and in the other two, less than 0.1

parts per 100 parts of polymer. The inference is that the anti-oxidant content of these rings, although initially adequate, had been reduced in service to an insignificant level, either by chemical oxidation, leaching by water, or by some other agency, perhaps micro-biological.

Two Australian and one New Zealand corroded sewerage rings were similarly analysed and it was found that in each case, the vulcanisate was of a poor quality formulation with low rubber content and low grade fillers but again with no persistent anti-oxidant. Of special significance was the fact that the copper content of each was high and in the case of the New Zealand specimen there was also a high manganese content.

A ring from a British source was examined and found to contain up to 200 times the usual amount of copper and its deterioration undoubtedly resulted from catastrophic copper-catalysed oxidation. In the other cases where it was present, the copper content, though not of this magnitude, was high enough to indicate that it could have been a major contributory factor in the subsequent deterioration.

Micro-biological Analysis

From all rings, with the exception of that of British origin with a very high copper content, isolations were made of *Actinomycetes* which were present as significantly large populations. These consisted usually of pairs of dissimilar individuals, one of which was grey-whitish and sporing, and the other buff-pink and relatively asporous when cultured on dextrose-peptone agar *(Figure 1)*. The first of these organisms was identified as belonging to the genus *Streptomyces*, while the second, which is notably pleomorphic, is probably of the same genus although possessing some features in common with the genus *Nocardia*. More precise identification is proceeding. These characteristic pairs of strains were morphologically similar to those isolated by LEEFLANG (1963), and indeed the superficial morphological conformity of such isolates from similar environments but from widely divergent regions of the world not only illustrates the remarkable ubiquity of the *Actinomycetes* but emphasises the circumstantial association of some species with corrosion of this type.

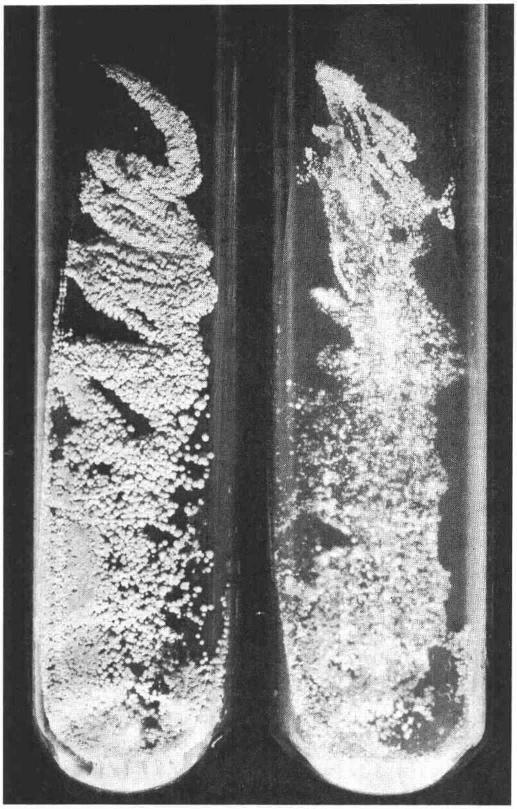

Figure 1. Two characteristically dissimilar species of Streptomyces *isolated from a slightly corroded Australian sewerage ring. That on the left is buff-pink in colour and relatively asporous, and that on the right, greyish white, sporulating.*

ROLE OF *STREPTOMYCES* SPP.

The published literature is notable for the wide range of micro-organisms credited with the ability to attack natural rubber vulcanisate, and recent publications list for example, *Aspergillus niger; A. glaucus; Aspergillus versicolor; Penicillium brevicompactum; Penicillium cyclopium; Alternaria tenuis; Paecilomyces varioti* and *Actinomyces* spp. (PETRUJOVA AND ZANOVA, 1960; RYCHTERA AND BARTAKOVA, 1963). The present investigations how-

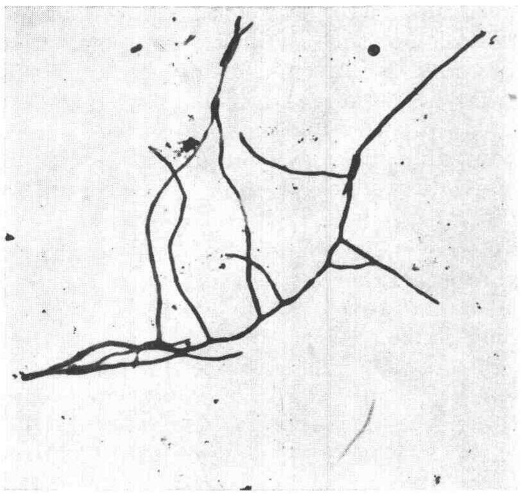

Figure 2. Hyphae of Streptomyces griseus *grown in submerged culture in a liquid medium. Electron micrograph × 2000.*

ever, confirm without doubt the view of LEEFLANG (1963) that micro-organisms belonging to the *Actinomycetes* are involved circumstantially in the reported cases of corrosion of natural rubber pipe sealing rings. This does not preclude the possibility of symbiotic relationships with other organisms from divergent orders, and this aspect is under investigation.

The genus *Streptomyces*, a group of organisms of fairly simple, yet obscure life-history (KLIENEBERGER-NOBEL, 1947; DICKENSON AND MACDONALD, 1955; WAKSMAN, 1961) is distinguished from bacteria by the ability to form filaments or hyphae, which are narrower than those of the mould fungi and which rarely exceed 1 micron in diameter *(Figure 2)*. Reproduction is generally by means of asexually produced spores but it is slow, and this, together with a slow growth rate places them at a disadvantage in competition with bacteria and fungi for simple, readily assimilable substrates such as sugars and amino acids, where speed of colonisation is necessary for survival. However, the frequency of occurrence of *Streptomyces* and other *Actinomycetes* in the complex flora of the soil is indicative of the possession of other facilities enabling them to compete successfully. The ability to produce antibiotics for example, is thought to be advantageous to them in mixed populations and in addition, they are able to deal with a wide variety of complex substrates, which resist decomposition by primary bacterial and fungal colonisers; thus their activities do not compete with those of such organisms which subsist on the simpler compounds.

Although the literature evidence concerning the presumptive micro-biological utilisation of natural and synthetic rubber hydrocarbons is factually conflicting, this is not so for hydrocarbons generally, for there exists a substantial volume of elegant work (reviewed by VAN DER LINDEN AND THIJSSE, 1965), which is concerned with pathways of micro-biological dissimilation of aliphatic and aromatic hydrocarbons, many of which may be partially or completely oxidised. Using highly purified substrates, refined techniques in chromatography and tracer isotopes, intermediates have been isolated and mechanisms firmly established. This has shown that all hydrocarbons are not utilisable, but that micro-organisms display a remarkable degree of selectivity towards them dependent on the scale of biological complexity of the organism and the nature of the hydrocarbon relative to its chain length and detailed structure. For example, *iso*-octane (2,2,4-trimethylpentane) is oxidised by certain soil and marine bacteria (STRAWINSKI AND STONE, 1940; ZOBELL *et al.*, 1943) although it is untouched by strains of the bacterium *Pseudomonas* (KONOVALTSCHIKOFF-MAZOYER AND SENEZ, 1956). Generally, the more advanced the organism is from the systematic aspect, the greater is its versatility and certain *Nocardia* spp. for example, which are closely related to *Streptomyces*, have been shown to consume pristane, squalene and squalane, all of which possess methyl branches of similar pattern to those which occur in natural rubber, while *Pseudomonas* is able only to consume squalene, and *Micrococcus* can utilise none of these substances (MCKENNA AND KALLIO, 1964). Generally however, from studies of straight and branched chain alkanes it has been found that the straight chains are easily oxidised by certain micro-organisms but that branched compounds must possess a sufficiently long unbranched chain in order to be attacked (THIJSSE AND DE VRIES, 1959).

Further, it is clear from these detailed researches that the oxidation is invariably terminal—at the ends of the molecule—at C_1 or C_6. From this, it follows that, although theoretically there is a possibility of attack by *Streptomyces* on the molecules of natural rubber, this may occur only at the ends, providing the organism is equipped with the extra-cellular enzymes specifically necessary to deal with totally water insoluble substances of small surface area. If this latter improbability were a fact, then any direct attack would be so slow as to be virtually undetectable and even then in the case of vulcanised rubbers, it could well be blocked by S cross-links and S main chain modifications. Thus, it will be seen that because of this inability to initiate points of attack *along* the hydrocarbon chains, the fact that micro-organisms, as far as is known, are unable to utilise directly long chain hydro-carbon polymers of high molecular weight is not unexpected. This suggests that a direct or primary micro-biological degradation of the intact natural rubber vulcanisate molecule is very unlikely.

It may be, however, that the association of *Streptomyces* with corrosion of NR vulcanisate is explicable by the possibility that the organism attacks by oxidation, not the rubber vulcanisate itself, but low molecular weight fragments produced by a primary, non-biological degradation following which many more terminal carbon atoms would be available, and that the presence of the micro-organism as a *secondary* feature may alter the course of this degradation—accelerating it, but not initiating it. This primary degradation may require molecular oxygen, because the unlikely alternative of a mechanism involving primary activity by *Streptomyces* implies additionally that the organism would have to possess an extra-cellularly active 'rubber oxidase' enzyme system capable of digesting insoluble rubber into utilisable low molecular weight fragments. Logic enters into these considerations, for the possession of such a system would imply that *Streptomyces* induced degradation underground would be rapid and commonplace and that natural rubber would be no more persistent in moist soil conditions than the readily decomposable insoluble cellulose and lignin residues of plant materials.

Corrosion of natural rubber vulcanisate however, is characterised not by its rapidity, but by its extreme slowness and, as has been found in the course of the N.R.P.R.A. investigations, by an initial lag phase of at least eleven months, and for some formulations, much more before its detectable onset, even *after* extensive and visible surface colonisation by *Streptomyces*. Such a long delay is consistent with the possibility that slowly developing non-biological changes affecting the rubber vulcanisate and causing a primary chemical degradation, in itself undetectable and of no practical significance precede a secondary biological degradation and that these changes require a variable time dependent on the local conditions and the nature of the vulcanisate formulations.

In support of this possibility, the analysis of corroded natural rubber rings referred to above indicate a notable absence of persistent anti-oxidant. This becomes a practical matter of significance if viewed in relation to the propositions of (a) the theoretical requirement for a primary degradation of the natural rubber molecule into fragments of lower molecular weight, (b) the presence of a prolonged lag period of varying duration before the onset of detectable surface corrosion, (c) the positive influence of variations in the nature of the vulcanisate formulation and (d) the influence of variations in the environment.

In the moist or wet conditions to which such rubber sealing rings are continually exposed, persistence of certain anti-oxidants is now known to be unlikely over any significant period in the long service life of the ring and their rapid disappearance may be caused by the effects of leaching or, on occasion, micro-biological activity. Leaching of some amine-based and phenolic anti-oxidants in rubber compounds can be very rapid and, indeed, experiments have shown that in the case of substituted *p*-phenylenediamines for example, substantial amounts are removed from the surface layers of tyre tread compounds during immersion in water for periods as short as 24 hours, and further, that the amount removed depends on the chemical structure of the substituents and the concentration of anti-oxidant present (LLOYD AND PAYNE, 1967). Fortunately the recent discovery in these laboratories of the principle of network-bound anti-oxidants completely resistant to leaching (CAIN *et al.*, 1969) indicates a positive method of eliminating this problem.

There is also a possibility of micro-biological degradation of certain of the amine-based and phenolic anti-oxidants in common use, for most *Streptomyces* spp are especially able to utilise primary and secondary amines as sources of nitrogen while many can oxidise phenolic compounds to quinoids (KÜSTER, 1963). Indeed, such is the complex nature of the various substances incorporated in a rubber vulcanisate that, in addition to the vulnerable anti-oxidants, there may be present other micro-biologically utilisable non-rubber fillers and additives: surface corrosion could be initiated by the presence of particularly susceptible components such as, for example, paraffinic hydrocarbons.

The water environment to which the rings are exposed must also play its part in the activities of *Streptomyces*, for the unusually high phosphate level in the dune waters of Holland clearly contributes to the ability of the organism to proliferate, and this is aided by the absence of deliberate chlorination: chlorine, although only bactericidal towards *Streptomyces* at a relatively high level could, at a low residual level, fulfil a non-biological role by being cumulatively absorbed on the surface of natural rubber vulcanisate thus producing a film of chlorinated rubber of molecular thickness, yet resistant to oxidation, and functioning to a greater or a lesser degree as a water impermeable barrier.

Such considerations as these, among others, have formed the basis of the N.R.P.R.A. testing programme now in progress. This has been designed in two consecutive parts, the first based on preliminary hypotheses and the second mainly on the results of the first.

EXPERIMENTAL

Following the procedure of LEEFLANG (1963) a simulated field test was established at the N.R.P.R.A. laboratories in December 1965. A number of specially devised formulations was tested for their reaction to immersion in the local mains water containing inocula consisting of, in each of two test tanks, (a) two strains of *Streptomyces* isolated from corroded Dutch water main rings and (b) two strains isolated from a corroded Australian sewerage ring. A replicate set of specimens was immersed in a third test tank in which as a control, there was no deliberately introduced *Streptomyces* inoculum. Concurrently, the same range of specimens was subjected to test in the laboratories of the North Holland Provincial Water Board, Bloemendaal, Holland, where they were immersed in the local unchlorinated mains water inoculated with the same two indigenous Dutch *Streptomyces* strains as those used in the Welwyn Garden City experiment.

The test formulations contained RSS 1 as base polymer and were designed (a) to provoke early corrosion in accordance with working hypotheses such as those explained above, by, for example, the total exclusion of anti-oxidant or the incorporation of varying levels of a range of conventional anti-oxidants; by the incorporation of copper as a contaminant expected to catalyse early chemical oxidation; by accelerated ageing; by the use of low grade rubbers and fillers etc., and (b) to protect against corrosion by general presumptive adequacy of formulation. Some conventional styrene butadiene rubber formulations were also included.

In addition, since chlorine was entirely absent from the dune waters of North Holland and other areas where corrosion occurred, yet was apparently influential in other areas in affording protection from it, certain of the specimens were subjected to deliberate surface chlorination prior to immersion, with the object of seeking reasons other than a direct bactericidal effect on *Streptomyces* for the absence of, or mitigation of corrosion in its presence.

At the present stage of this experiment, the following facts have been established:

1. Under English conditions, corrosion of a small proportion of natural rubber specimens was first detectable after eleven months immersion in each of the two tanks containing the Dutch and Australian *Streptomyces* inocula. However, although its initiation was practically simultaneous in each tank, the pace of it was more rapid in the presence of the Dutch inoculum. Despite this, there was eventually almost complete conformity between individual formulations in the two tanks in the possession of a positive or negative reaction.

Corrosion did not occur on any specimen in the control tank.

2. Comparison between replicate specimens tested under Welwyn Garden City conditions and Dutch conditions both with the Dutch *Streptomyces* inocula showed that the onset of corrosion in a few specimens appeared much earlier in Holland—at about four months—than in England, and that once an apparently linear progression of surface corrosion was established, it was about thrice as rapid. Again there was general conformity in the performance of replicate specimens on test in Holland and England under the two different environmental conditions.

3. Individual formulations with adequate anti-oxidant protection behaved generally in accordance with expectation and the initiation of corrosion was usually delayed by a factor corresponding to increasing content.

4. Surface colonisation by *Streptomyces* was found to be non-selective for type of vulcanisate or base polymer since, in the English conditions, two strains morphologically similar to the introduced inocula were usually visibly growing on, and could always be isolated from the surfaces of all specimens in the test tanks, including all SBR specimens, irrespective of whether or not corrosion symptoms were present.

5. No surface corrosion was found on the SBR specimens under these conditions, thus endorsing the expectation of the need for a specifically adapted or selected organism to achieve it.

6. The incorporation of paraffin wax into formulations induced early surface degradation of bloomed wax with an associated increased susceptibility to vulcanisate surface corrosion.

7. Surface chlorination of specimens conferred complete immunity to corrosion under both Dutch and English experimental conditions.

CONCLUSIONS

The facts emerging from these experiments and from those of a similar nature conducted elsewhere are not inconsistent with the possibility that non-biological agencies concerned with potentially deleterious chemical and physical changes in the surface layers of the specimens may be involved in the complex of factors governing the ability of *Streptomyces* to proceed from the role of passive surface coloniser to that of an active, though slow utiliser of surface degradation products. Relevant to this is the fact that corrosion is rarely of deep penetration but is limited to a slowly renewing fresh rubber surface even though *Streptomyces* has been shown by LEEFLANG (1963) and also by work in these laboratories, to ramify and proliferate in the undegraded inner material of surface corroded rings, presumably through micropores left by the removal of filler materials.

Unless ring compounds contain chance, or deliberately chosen inhibitory materials, such as fungicides—and these would usually be vulnerable to leaching over a prolonged service life—surface colonisation by *Streptomyces* is inevitable, for long term immersion in water or sewerage fluids implies that, if the environment is acceptable in terms of hydrogen ion concentration, oxygen concentration, nutrient salts and available sources of nitrogen etc., then micro-organisms will colonise available surfaces bearing films of utilisable organic matter. This may be general organic debris including the remains of surface adherent organisms such as bacteria, moulds and protozoa or, as is postulated above, primary chemical degradation products of the rubber, or utilisable additives.

Recognition of these factors and of the probability that natural rubber vulcanisate, if unaffected by non-biological environmental factors, is theoretically unlikely to be utilisable as a carbon source by micro-organisms, indicates that adequate protective measures are possible when all conditions are understood.

Here, however the extremely slow progress of corrosion under service conditions and simulated field test conditions is equally a reassurance and a hindrance, for where days would be desirable, at present, months are necessary for the evaluation of hypotheses. Experiments are in progress using sophisticated laboratory techniques which, it is hoped, may enable a direct and rapid assessment of trial formulations to be made. This is clearly desirable, for although the promise of complete protection emerges from certain of the treatments included in the first test series, it is inappropriate to make practical recommendations until full confirmation is obtained.

From the facts so far established, a new series of formulations has been prepared and these are now under examination, as before, under both English and Dutch conditions. More information is required, for example, about the proven deleterious nature of paraffin wax incorporation—a substance whose inclusion is now contra-indicated—and the level at which, free chlorine in potable waters is a factor affecting the prevalence of field corrosion. Using an attenuated surface reflectance method it has already been found that, under Welwyn Garden City conditions of prolonged test immersion, surface changes take place in uncorroded natural rubber vulcanisates which are consistent with mild chlorination. Such changes can only have occurred by cumulative adsorption with time of chlorine present in the water at the very low level of 0.4 p.p.m., and this finding, together with the fact of total immunity conferred by deliberate surface chlorination, suggests that a trivial chlorine content may be one of the reasons for the much slower pace of corrosion under English as compared with Dutch test conditions on those specimens where it occurred.

Further, the processes of leaching, particularly of different anti-oxidants, in relation to susceptibility to corrosion is under study, and included in these investigations are examples of the novel network-bound anti-oxidant formulations (CAIN *et al.*, 1969) which are totally immune to removal of anti-oxidant during conditions of permanent immersion in water. Relevant too is the susceptibility of certain anti-oxidants to bio-deterioration, and means of inhibiting this process are also under study.

The subject of bio-deterioration of industrial materials is assuming major importance with the ever increasing use of synthetic substances novel to the attentions of micro-organisms which can, however, by mutation and selection and/or adaptation acquire the ability to degrade unusual substrates provided the molecular configuration is, or becomes acceptable. This may not be, and indeed, usually is not a rapid process, as is exemplified by, for example, the relative infrequency of reports of micro-biological degradation of synthetic rubber compounds and the fact that when they are tested over short periods against micro-organisms selected from other substrates they are unaffected. However, in situations where the micro-biological flora is varied, as in soil burial tests, instances of bio-deterioration of, for example, silicone rubber sealants (CALDERON AND STAFFELDT, 1965) have been reported and retrieved field examples of susceptibility in other synthetic rubbers will, it may confidently be predicted, become more frequent as time progresses and usage increases. At present broad claims of inherent immunity to bio-deterioration of synthetic rubbers are unrealistic.

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DISCUSSION

Chairman: Dr. W. F. Watson

Mr. D.H. Taysum mentioned the review by C.E. ZoBell indicating widespread microbial degradation of polymeric hydrocarbons, both natural and synthetic. Dr. Dickenson agreed that ZoBell's review was excellent; however, that was 25 years ago and more information was now available in this rapidly changing field. Also, caution was necessary in applying laboratory results to service conditions. Unless the substrates were chemically pure and well identified, uptake of oxygen in laboratory experiments was inadequate evidence of microbial consumption of natural or synthetic rubbers.

Mr. Taysum said that he had found rapid decomposition of unvulcanised rubber when buried in Malayan soil. Dr. Dickenson said these findings agreed with those in his paper although most of his data dealt with vulcanised material. Unvulcanised material usually contained utilisable substrates such as protein.

Dr. A.A. Watson suggested exposure of highly oxidised vulcanisates to *Streptomyces* to test whether microbial degradation of natural rubber was necessarily preceded by an induction period of molecular weight reduction. Dr. Dickenson said preliminary investigations of this nature proved inconclusive; for instance, no significant differences between the rates of microbial activity towards vulcanised and oxidised vulcanised natural rubber latex had been found. He attributed this to the difficulties of conducting biological experiments on very slow processes.

Mr. J. Payne said his work on synthetic detergents indicated that the configuration of the hydrocarbon chains influenced the rate of degradation. Straight chains were attacked much more rapidly than branched chains. Different molecular configurations might therefore give rise to very big differences between the various hydrocarbon polymers and between NR and SBR. Dr. Dickenson agreed with this view; it was also irrational to test synthetic rubbers with organisms adapted to natural rubber and its derivatives. Perhaps certain synthetic rubbers would be degraded when sufficiently exposed to organisms in the soil, capable of appropriate adaptation.