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Electrochemical Degradation in Rubber

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Micrographs are shown of some typical types of structural damage that can occur in a vulcanisate as a result of electrochemical degradation (ECD) in the material. The importance of the carbon black content, the operating temperature, the coolant composition, a vulcanisates cure system and other compound ingredients on the size of the current that can flow through a vulcanisate and its impact on ECD were discussed as well as the effects of crosslink density on volume resistivity and current flow. Results from SEM X-ray analysis of ECD damaged material on the depletion of zinc and sulphur by ECD and the associated effects on current flow through a compound are also discussed.

Keywords: electrochemical degradation; structural damage; vulcanisate; analysis

Electrochemical degradation (ECD) can take place in rubber vulcanisates that are in contact with a metallic component and a liquid. Contact between a reactive metallic material such as aluminium, a rubber compound and a liquid electrolyte can in effect form an electrical cell. Under these conditions the rubber component can have an electrical current passing through it which may generate ECD leading to damage within the rubber and potential failure of the rubber component.

One of the most common situations where ECD can occur in a rubber component is in a hose used in automotive cooling systems[1–5]. Contact between a rubber hose, an aluminium engine component and the liquid in a vehicles cooling system can form an electrical cell as the coolant liquid can act as an electrolyte and an electrical current may pass through the hose that can make it susceptible to ECD. Hose compound can typically contain a relatively large amount of carbon black filler. This type of compound combined with the high operating temperatures found in a vehicles cooling system can exacerbate a hoses susceptibility to ECD. ECD has been recognised since the mid 1980s, however, in recent years the steady trend towards increased under-bonnet operating temperatures in automobiles, an increase in the use of aluminium engine components and changes in coolant additives have tended to increase the likelihood of ECD taking place in a hose. Studies on the modes of failure taking place in automotive coolant hose have shown that ECD has now become a major cause of hose failure.

EXPERIMENTAL

The ECD measurements reported here were conducted either with a series of identical beaker cell test apparatus or a Brabolyser type

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hose test apparatus. An example of a beaker cell apparatus is shown in *Figure 1* with a rubber test piece held in a clamp and partially immersed in a coolant fluid. Each beaker cell had two clamped test pieces spaced a set distance apart. These test pieces could consist of one metallic electrode and one rubber test piece or two rubber test pieces. Each test piece in a beaker cell consisted of a flat rectangular shaped sample of 100 mm by 10 mm and 2 mm in thickness cut either from moulded rubber sheet or metal sheet. A typical test procedure would be to clean and then weigh each test piece before fixing them in the metallic clamps and immersing in a coolant within the beaker with the coolant pre heated and maintained at the desired temperature. The voltage and current flowing across the test pieces would be continuously monitored throughout a test. Test pieces would again be weighed normally immediately following a test in order to determine the amount of weight change of a sample. The weight change of a sample can indicate the degree of swelling of the sample by the coolant which can be indicative of the amount of ECD damage in the specimen as ECD damaged material typically retains a substantial amount of fluid. Similar test pieces were also immersed in coolant under identical test conditions to the ECD tests, but without a flow of current, to provide a control for comparative mass uptake purposes. These control test pieces would normally show much less mass uptake than ECD damaged material. Sectioned test pieces were also prepared for SEM examination and micrographs taken of swollen and ECD damaged regions within the rubber. In the case of the tests with one metallic electrode and one rubber test piece the current and voltage flow was normally supplied by the potential difference generated between the two test pieces in the cell itself although a voltage could also be applied by an external power supply if desired. Where two rubber test pieces were present an external power supply was required to generate a current flow across the test pieces, here one test piece effectively acted as an anode and the other as a cathode. The current flow, which under some conditions can be very small, was measured by a purpose built zero impedance ammeter which was capable of measuring the very small currents present. The time duration of a test could vary widely depending upon the particular test conditions. A short-term test to measure the current flow across a rubber compound and a metallic electrode could be satisfactorily completed in about 30 minutes whereas the production of some test pieces with sufficient ECD damage for microscopic examination could take a month or more.

The second type of apparatus constructed was for ECD testing of sections of hose. This comprised two sections of test hose fixed between a glass tube that was filled with liquid coolant or a single section of hose with an aluminium rod of circular cross section fixed centrally within the glass tube filled with coolant. The resulting current flow was again monitored with a zero impedance ammeter in a similar manner to the beaker tests.

Measurements of the change in the current taking place over time in a cell test held at a constant temperature have shown that following the thermal equilibrium of a test piece the current can increase a little over the short term and may pass through a peak value usually after some 10 to 40 minutes of testing depending upon the material and the test conditions. Over a longer time, the current once passing this peak value can progressively fall until an equilibrium condition is reached and the size of the current remains relatively constant. With the test apparatus and conditions investigated here, the equilibrium condition could be reached after some 12 to 24 hours and the size of the current under this steady state condition can remain smaller than the current at the beginning of a test. Short-term measurements of the current produced in a

Figure 1. A typical ECD beaker cell test apparatus partially filled with a coolant with a rubber test strip shown in the foreground attached to a fixing clamp for electrical connection.

cell test with different rubber compounds under otherwise similar test conditions can be useful for quickly providing a relative indication of different materials susceptibility to ECD. Longer term cell tests can be more suited to steady state measurements and the production and examination of ECD damaged material.

RESULTS AND DISCUSSION

Some Physical Effects of ECD Damage

ECD can produce weak regions within a rubber compound or tube wall in the case of a hose where cracks can propagate through the material more easily than in undamaged areas. ECD can also affect the structure of a rubber compound and form characteristic structural damage sometimes called striations. Initially these cracks and striations normally develop within the interior of a vulcanisate and may propagate towards the surface of a component such as a hose wall leading to pinhole leaks of coolant and degraded regions of material often near one or both ends of a hose close to a connection point. Rubber compound close to an air and liquid coolant interface can be particularly susceptible to ECD and this can make the top hose in an automobiles cooling system most at risk to ECD.

An example of the type of structural damage ECD can produce through a sectioned sample of EPDM hose compound is shown in *Figure 2* at intermediate magnification. The central horizontal dark coloured strip is part of a crack running through an ECD damaged region of material while either side of this crack typical ECD damage or striations can be seen. At the upper and lower part of the micrograph undamaged material is also shown.

A further example of the type of structure that can occur in a vulcanisate due to ECD damage is shown in *Figure 3* at a higher magnification. The striations can be seen to consist of a porous sponge like structure

containing many voids. Some undamaged material is also shown mainly towards the lower section of the micrograph. ECD damage while normally initially occurring within the interior of a vulcanisate may be detected at the surface of a material when the damage has reached a sufficiently advanced stage. The sponge like ECD damaged structure of a material similar to that shown in *Figure 3* can allow considerable liquid or coolant ingress into these regions and the material may experience quite a large degree of swelling. Such ECD damaged areas that occur near the surface of a component can lead to relatively highly swollen regions or blisters forming at the surface of the material. *Figure 4* shows an example of one such blister that has developed on the inner tube of an automotive coolant hose. The blister shown protrudes some 5 mm out from the tube surface and may reach a sufficient size to impede coolant flow through the hose. If the hose is allowed to dry in air such blisters can exude coolant for a number of days and may partially collapse as seen in the photograph. Exuded coolant can occur at specific positions at the surface of a material where striations have reached the surface and coolant droplets can form at these points over time. The presence of these droplets of coolant can provide a useful means of identifying the exact position of ECD damaged material as otherwise the normally localised and mainly internal ECD damaged regions can be difficult to identify.

SOME FACTORS AFFECTING ECD

Carbon Black Content and Temperature

The resistivity of a vulcanisate will influence the size of the electrical current that may flow through the material. Current flow can be linked to the degree of swelling and ECD damage occurring in a given vulcanisate while the size of the current flow itself can also be strongly influenced by the conductive qualities and loading of the carbon black filler in the compound. With low loadings of carbon black the current that can pass through a compound can be minimal but as carbon black loadings rise there can be a corresponding increase in the current flow. Carbon black loading and type is therefore a very important factor in governing a materials susceptibility to ECD damage. The operating temperature of a cell can also have a further important influence on the current flow in a compound. An increase in the operating temperature normally leads to an increase in the current flow through a material.

Figure 5 shows an example of the variation in the size of the current that can take place through an EPDM based vulcanisate with carbon black loadings ranging from 55 to 120 parts per hundred (p.p.h.r.) at temperatures of 50, 65 and 80ºC. The data includes two different grades of carbon black, N990 at the 95 p.p.h.r. loading level while the remaining loading levels are N550. The carbon black grade is seen to influence the size of the current in the vulcanisate as well as the carbon black loading. The lower structure N990 carbon black tends to give a smaller current flow than the higher structure N550. At the lower carbon black level of 55 p.p.h.r. or 30% volume loading there is relatively little current flow taking place at any of the test temperatures and these materials are likely to have a low risk of sustaining ECD even at the higher operating temperatures. With an increase in the carbon black level and the coolant temperature the current flow in a material can increase significantly and the susceptibility of these compounds to ECD is increased. Hose in automotive cooling systems can operate at temperatures of some 100ºC and there will be a corresponding increase in the current flow through a hose compound and greater susceptibility to ECD as the temperature increases.

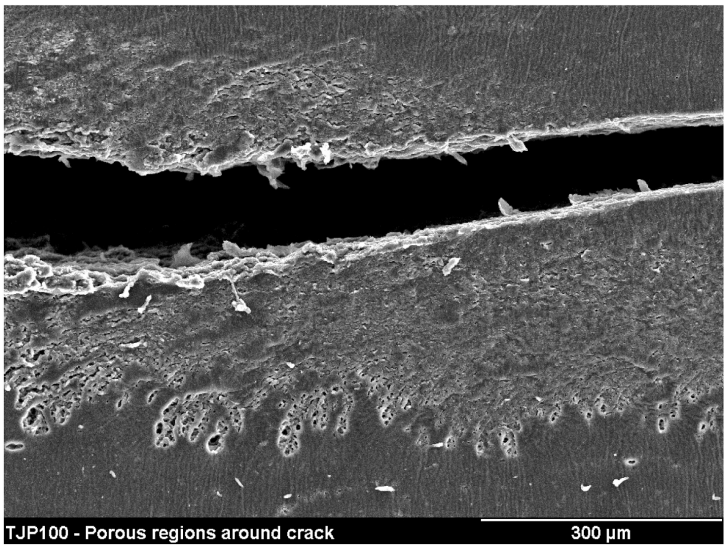

Figure 2. Showing ECD structural damage in a vulcanisate either side of a horizontal crack caused by ECD at a medium magnification. Undamaged rubber is also shown at the top and bottom of the micrograph.

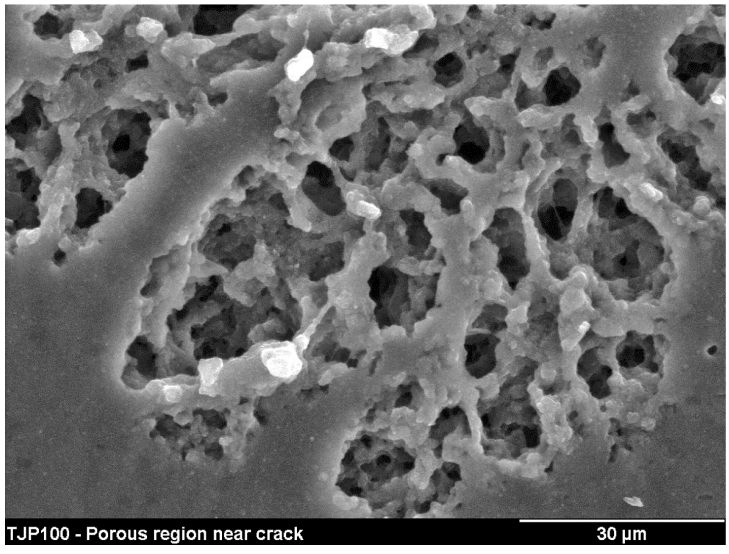

Figure 3. Showing ECD structural damage at a higher magnification. The weak damaged regions of the rubber can consist of a sponge like structure containing many voids.

Figure 4. Showing a section of rubber hose after exposure to ECD. A "blister" has formed on the inner wall due to the ingress of liquid coolant into the rubber as a result of ECD.

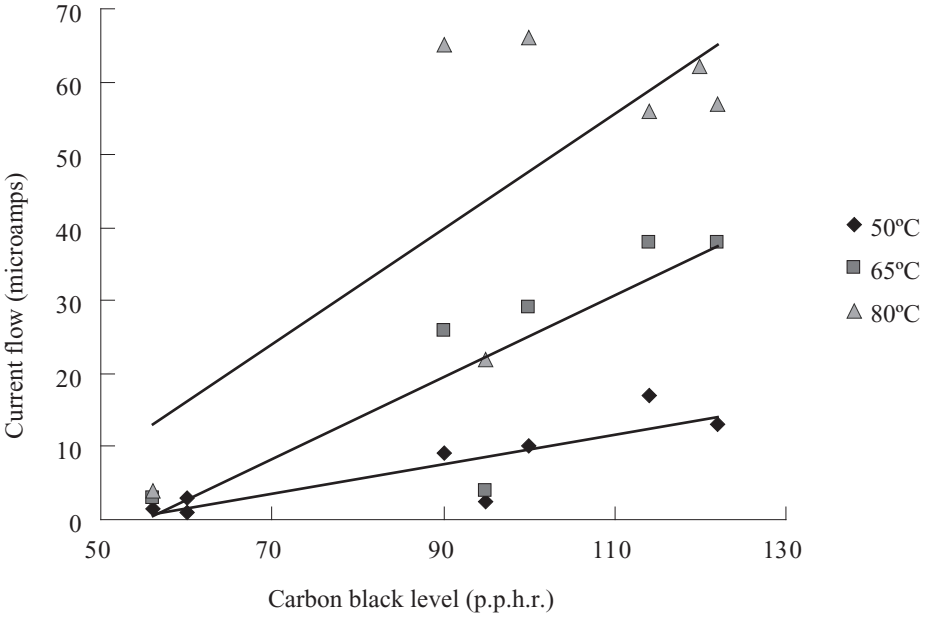

Figure 5. Current flow versus carbon black levels at three coolant temperatures. N990 grade carbon black is shown only at the 95 p.p.h.r. loading, the remaining loading levels are N550 grade.

Electrical Current and Temperature

The size of the electrical current that can flow through a vulcanisate is an important parameter in determining the susceptibility and rate of ECD in a material. The current flow can also be strongly affected by the operating temperature of a cell or hose assembly. The size of the current flow through a rubber compound will normally increase as the temperature increases. However, this increase in the current does not remain linear over a temperature range between ambient and the boiling point of the coolant, but rather can have three phases or rates of change.

Figure 6 shows an example of the three phases of the change in the current with temperature in this case in an EPDM peroxide cured vulcanisate containing 120 p.p.h.r. N550 carbon black, 60 p.p.h.r. process oil and no zinc based additive. A lower current transition point occurs at a temperature of some 70ºC and below this point the current remains relatively small and alters only a little with a change in the temperature. The susceptibility of a compound to ECD is therefore likely to remain low at temperatures below this transition point and over prolonged periods of time at ambient temperature when an automobile may for example be at rest. The lower current transition point was found to occur at nearly the same temperature with all the different compounds, varying filler types and filler loadings in the EPDM vulcanisates tested here. The temperature of the lower current transition point therefore appears largely unaffected by compounding ingredients such as fillers. The mechanism responsible for this lower current transition point has not been determined, but it does appear to be temperature related and it is normally triggered when a temperature of approximately 65 to 70ºC is attained. It is of interest to note that this lower temperature transition point does coincide quite closely with a temperature when significant additional crosslinking can begin by the normal thermal maturation process and an increase in the crosslink density will normally lead to an increase in the current flowing through a material. Over a temperature range between the lower transition temperature and just below the boiling point of the coolant, the size of the current and the rate of change of the current with temperature can be considerably greater than that at lower temperatures below the transition point. A further current transition point can takes place when the coolant liquid just begins to boil. At this upper transition point the rate of the increase in the current with temperature can be raised still further and the size of the current can continue to increase as boiling of the coolant becomes more vigorous. The agitation produced by the gases in the coolant liquid on the electrode and rubber specimen when boiling takes place appears to enhance the current flow through the rubber. The compound ingredients in a vulcanisate can in some cases blur the sharpness of the temperature transition points shown in *Figure 6* but the underlying behaviour still remains. The much greater rate of change in the current taking place at higher temperatures does indicate that rubber components such as automotive hose that may operate at a temperature of only a few degrees higher than normal or intended can experience a significant increase in the current through the component and therefore a correspondingly greater susceptibility to ECD. The trend towards higher under-bonnet operating temperatures in automobiles can also be expected to have a similar affect on hose.

Thermal Cycling

While the size of the electrical current that can flow through a vulcanisate may increase with a rise in the temperature as seen in *Figure 6*, the thermal history of a material can

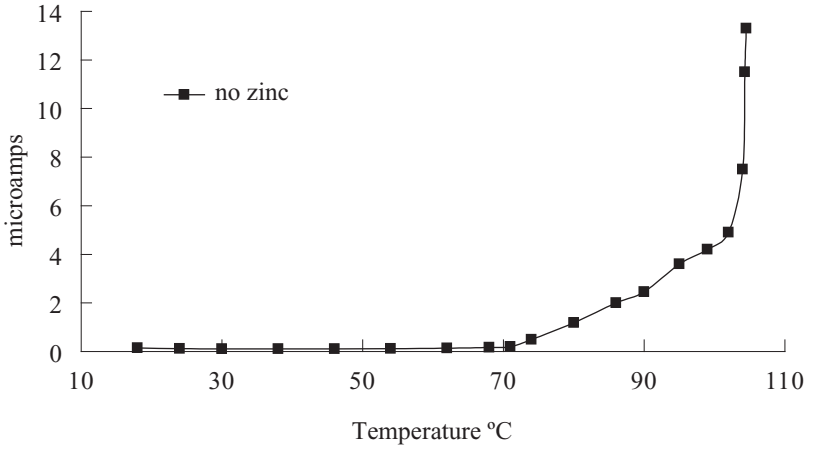

Figure 6. The ECD current in an EPDM peroxide cured vulcanisate versus temperature showing three distinct current phases.

also have a significant impact on the current flow through a material and therefore the materials' susceptibility to ECD.

Figure 7 shows an example of the type of variation in the current that can occur when a material is subjected to thermal cycling. The new virgin EPDM test piece shown has been subjected to four repeated thermal cycles between a temperature of 23 and 92ºC. Each thermal cycle was begun at the lowest test temperature, the temperature was then increased to the maximum temperature and then allowed to fall again to the minimum temperature. Each cycle was conducted over a period of eight hours. This provides sufficient time for the test piece to reach thermal equilibrium before each current measurement. With the exception of the initial first cycle data points, the lower line of each thermal cycle with the smaller current flow is the rising temperature half cycle and the higher current flow the temperature fall. The maximum current is seen to increase with each successive thermal cycle and the width of the "hysteresis" loop can become broader. This broadening of the hysteresis loop can lead to a significant increase in the difference between the rise and fall current at a given temperature and in particular at intermediate temperatures as seen in *Figure 7* at temperatures between some 60 to 80ºC. Under these conditions the fall current is therefore likely to contribute more towards any ECD taking place in a vulcanisate than the rising current. Following an initial thermal cycle, subsequent thermal cycles can have little further impact on the size of the current at lower temperatures and this low temperature current can remain quite small below temperatures of some 50ºC with a minimal risk of ECD occurring while a material remains at ambient temperatures. The increase in the maximum current flow seen per thermal cycle is thought to be at least partially due to further maturation or crosslink formation as a result of the continued thermal exposure of the vulcanisate and as such this increase in the maximum current may subside over time.

Electrode Material

The reactivity and ionisation properties of the electrode material is of fundamental importance to ECD in rubber as these properties will generate and influence the current that may flow through an electrical cell or hose assembly. For ECD in automotive hose applications, the main metal of interest is aluminium and its alloys as this material is found more and more frequently in modern engine blocks and ancillary automotive components. Aluminium based materials are also one of the more reactive metals and can therefore generate a relatively large current flow in a cell or hose which can make a rubber component susceptible to ECD. While the majority of the ECD tests conducted here were with aluminium electrodes, it is nevertheless of interest to compare the size of the current achieved with an aluminium electrode to that of some other metallic materials and put the current produced with aluminium in perspective with these materials. *Table 1* shows the current flow achieved in a cell test on EPDM peroxide cured hose compound with various electrode materials but otherwise under identical conditions. The cell tests were conducted at a temperature of 80ºC with the same proprietary automotive coolant.

A much greater reactivity and current flow is seen to occur with the aluminium than in the other metals and this illustrates why ECD

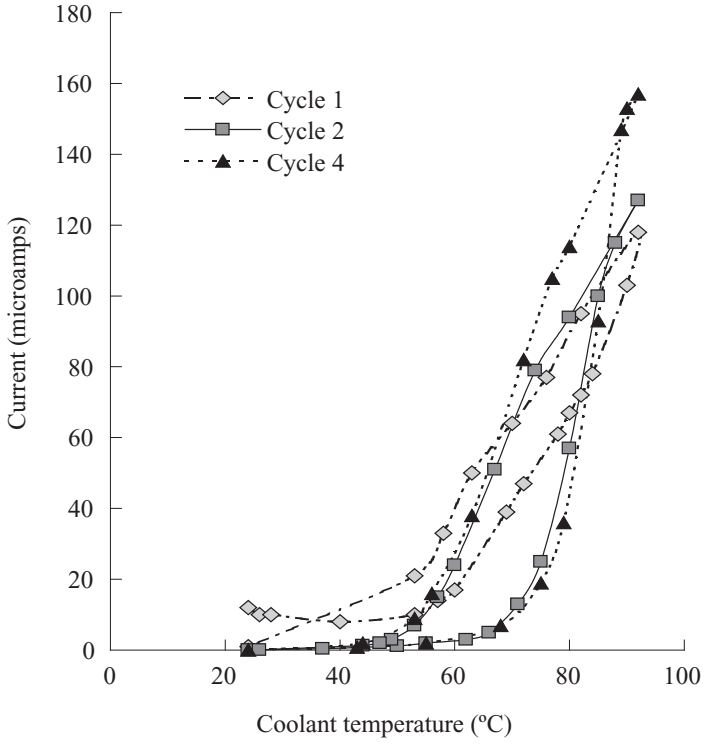

Figure 7. The coolant temperature versus current flow per thermal cycle, showing the variation in the current through a vulcanisate as a result of repeated thermal cycling.

can be such a problem in components such as hose in aluminium based automotive engines. The metal annealing process can also enhance current flow as seen with the zinc electrodes.

Liquid Uptake and Material Loss

When a rubber compound is in contact with a liquid, some liquid ingress can occur which will swell the rubber. With EPDM hose compound this swelling normally remains quite small and can be limited to only a few percent by weight at most. This degree of swelling will have little impact on the physical properties of a rubber compound and is quite acceptable in a hose. Where ECD is present in a rubber compound the degree of liquid ingress and swelling can be very much greater than in a material with no ECD. Significant swelling can lead to crosslink breakage and a general deterioration in the physical strength properties of the rubber compound. Gross increases in the weight of hose test pieces by liquid ingress when ECD is present can reach values of some 20 to 30% or more. As ECD is normally quite localised within a component the degree of swelling taking place at the actual ECD sites can be quite considerable and this swelling may well be sufficient to cause crosslink breakage and a permanent loss to the materials physical strength. A loss of essential ingredients necessary for the curing or maturation process of sulphur cured compound can also take place at the ECD sites and this loss is likely to inhibit any crosslink recombination that may otherwise take place thereby exacerbating any loss in a materials strength due to swelling.

The amount of material that can be lost in a hose compound by leaching or extraction by the liquid coolant passing through it normally remains quite small and acceptable in a compound not experiencing ECD. Peroxide cured vulcanisates in particular show low levels of leached material as there is little leachable matter present to begin with[6–9]. Sulphur cured compounds can have a little more leachable material than a peroxide cured compound as some unbound sulphur curative ingredients can be present which may be leached out, but this loss of material is normally quite small and can be minimised by a suitable choice of compound with an EV or semi EV cure system. Where ECD has occurred, the quantity of leached material can be greater and may include processing oil that is normally present in relatively large amounts in EPDM hose compounds. Process oil can be electrically non-conducting and the loss of quite small amounts of this material by leaching or extraction can reduce the resistivity and increase the size of the current flow through a compound. Such a fall in the resistivity is likely to increase the materials susceptibility to ECD.

TABLE 1. THE CURRENT GENERATED WITH DIFFERENT METALLIC ELECTRODE MATERIALS IN A CELL TEST

Electrode Material	Current (microamps)
Aluminium	58
Copper	4.6
Zinc	6.3
Zinc Annealed	19.3
Wrought Iron	0.7

Figure 8 shows the change in the current flow versus weight loss through two EPDM compounds each containing 120 p.p.h.r. of N550 carbon black and 60 p.p.h.r. 2280 process oil. The other ingredients in the compound are the same except one compound has a sulphur and the other a peroxide cure system. The majority of the reduction in the weight of the material is due to a loss of the process oil. Quite a small loss of the parafinic process oil is seen to cause an increase in the current flow in both the sulphur and the peroxide cured material, while the peroxide cured compound generally produces a smaller current flow than the sulphur cured material. The peroxide cured compound would be expected to have better resistance to ECD than the similar sulphur cured compound.

The Coolant

The composition of the electrolyte or coolant liquid in an automotive coolant system is an important factor in the electrochemical process and can significantly influence ECD in a rubber hose. The conductivity, inhibitor elements and pH of a coolant may all influence ECD. Coolant manufacturers now produce organic acid technology (OAT) coolants and while these can be more expensive than "traditional" coolants, these OAT coolants can give improved ECD resistance. Ethylene glycol is found in many proprietary coolants and is itself an electrically non-conducting material. A higher concentration of ethylene glycol can inhibit the electrochemical reactions taking place in a cell and an increase in the concentration of a coolant in a system can reduce current flow and thereby a rubber compounds susceptibility to ECD.

Figure 9 shows the increase in the weight of test pieces made of the same rubber compound immersed in six different proprietary coolants and tested in a beaker cell for ECD resistance under otherwise similar conditions. The coolant was maintained at a temperature of

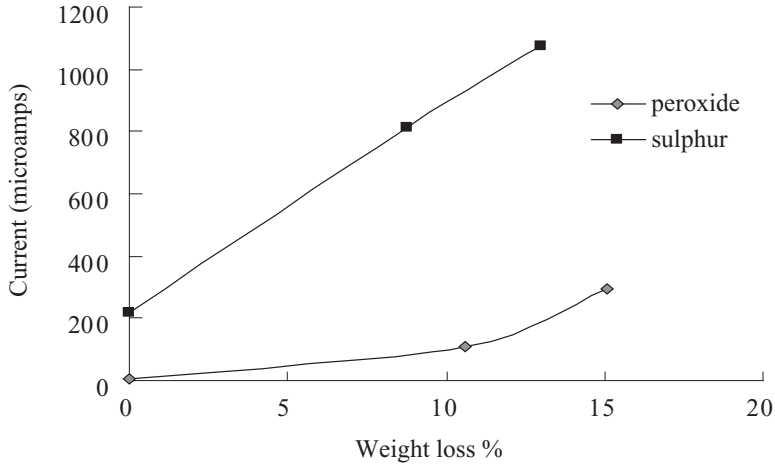

Figure 8. Material weight loss by acetone extraction versus current flow in EPDM, showing the increase in the current through a vulcanisate as a result of extracted material, mainly process oil.

80ºC throughout each test. The increase in the test piece weight is due to the ingress of coolant mainly as a result of ECD. A larger weight gain is indicative of greater ECD in a test piece. For the six proprietary coolants shown, the increase in the weight of the test pieces is seen to vary by a factor of about three. The six proprietary coolants were chosen to give only a representative cross-section of the traditional and OAT coolants available. The trade names of each coolant in consecutive order from 1 to 6 are; Top1, Comma Extreme, Mobil, Halfords Advanced, Eontech and Comma Super Coldmaster.

Ion chromatography measurements on proprietary coolants indicated the coolants consist of broadly three different types. These types are based on either a traditional formulation, an OAT formulation or a coolant apparently intended primarily as a topping up fluid. All the traditional formulations investigated contained nitrate while most also contained benzoate and some included phosphate. One coolant, Top1, had no benzoate or phosphate detectable and only low levels of nitrate but did contain a relatively high concentration of nitrite. The only significant cation present was sodium

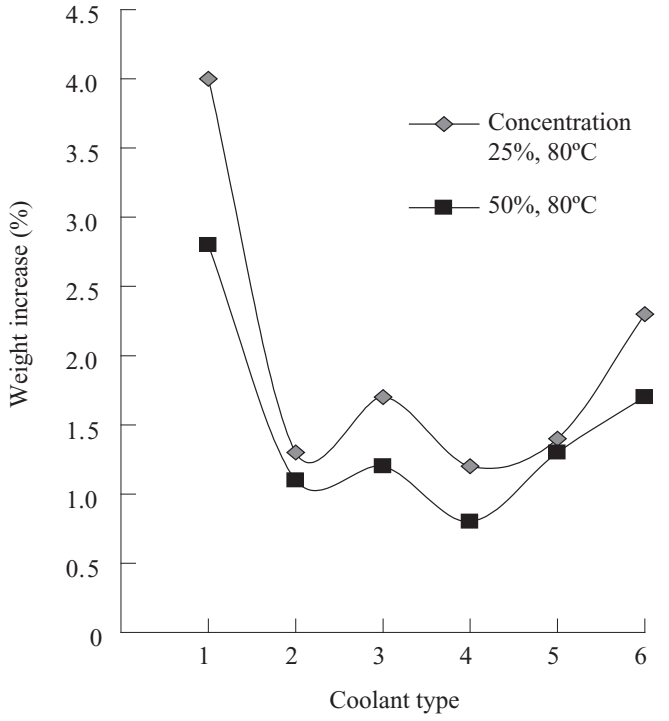

Figure 9. Test piece weight increase in six different coolants at 25% and 50% concentration in H_2O. ECD tests showing the variation in the mass uptake of a vulcanisate immersed in different proprietary coolants.

except in one coolant that had a 2:1 ratio of sodium to potassium. The OAT coolants tested were based on the presence of relatively high molecular weight dicarboxylic acids. All these OAT coolants contained adipate, sebacate, eicosane dicarboxylate and dodecane dicarboxylate. The only cation present in these solutions was sodium. All of the OAT coolants tested had a very similar formulation. The topping-up fluid consisted essentially of only diluted ethylene glycol and a colourant with no detectable corrosion inhibitor package or buffer chemicals.

The results illustrate that a coolant with a suitable composition can significantly reduce the degree of ECD taking place in a vulcanisate and that an increase in the concentration of a coolant, in this case from 25 to 50%, can further improve ECD resistance. Some of the proprietary coolants in *Figure 9* are OAT coolants while the remainder are traditional formulations. The dicarboxylic acid based OAT coolants 2, 3 and 4 can give improved ECD resistance over the traditional formulations.

Zinc and Current Flow

Cell measurements of the current produced with EPDM sulphur cured compound have indicated that the zinc oxide used for the cure process can give some increase in the current flow through these materials. The complexity of the chemical reactions taking place during the maturation of sulphur cured vulcanisates does, however, leave any role zinc may have on current flow difficult to quantify. Zinc loading and the presence of fatty acids, which can form a complex with the sulphur and stearic acid, are likely to affect the maturation and crosslink density which in turn can have a strong influence on the current in a material. It can therefore be difficult to determine any impact zinc itself may have on current flow from that of the effects of maturation on the current. Cell measurements of the current flow in peroxide cured EPDM hose compound with and without zinc have however shown that the presence of the zinc can increase the current through these materials as the zinc itself does not play an active role in the maturation process.

Figure 10 shows the current obtained in a cell test at different temperatures with an EPDM compound containing no zinc and with various different types of zinc. The EPDM compound contains 120 p.p.h.r. N550 carbon black and 60 p.p.h.r. 2280 process oil and is cured with 3 p.p.h.r. peroxide. The zincs tested have a wide range of melting points (MP). Zinc oxide (MP 1975ºC) and zinc stearate (MP 118–131ºC) will remain as a solid over the range of temperatures investigated here (some 20–105ºC) while zinc oleate (MP 85–65ºC) will change from a solid to a liquid and zinc hexanoate (MP -47ºC) will remain a liquid as the temperature is increased. In both the liquid and solid states, the various zincs produce an increase in the current when compared to the compound with no zinc present. The zinc oleate produced a small increase or spike in the current at its melting point of 85ºC and a few degrees either side of this temperature, but this spike in the current at the point of the phase change remains relatively small in comparison to the size of the change in the current over the range of temperatures investigated. In a similar manner to that of the enhancement of the current by the zinc in a peroxide cured vulcanisate, the zinc itself in a sulphur cured vulcanisate may also be responsible for an increase in the current as well as promoting maturation and any current associated with crosslink formation in a sulphur cured system. The lack of zinc in a peroxide cured vulcanisate may therefore be partially responsible for the better ECD resistance of these materials when compared to a vulcanisate that is sulphur cured.

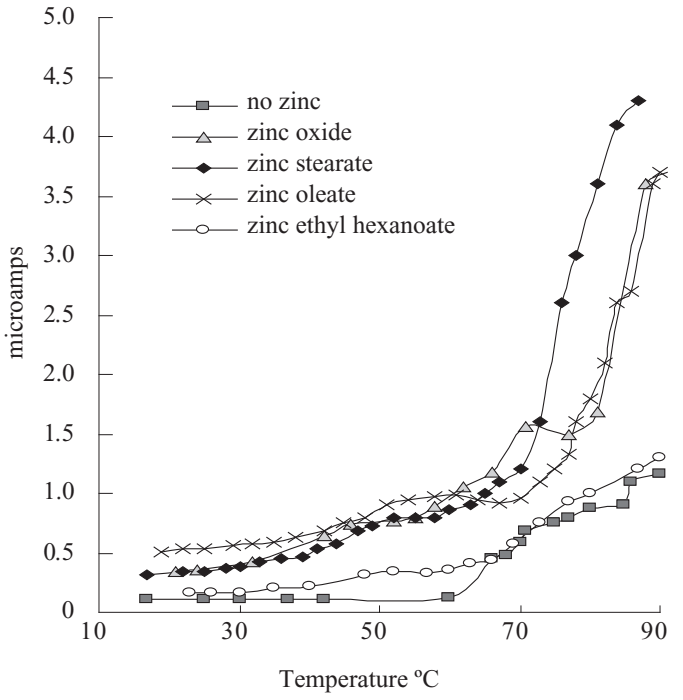

Figure 10. The ECD current versus temperature in EPDM compound, showing the effect of different zinc additives in a vulcanisate on the current flow over a range of temperatures.

A zinc electrode can produce moderate reactivity in a cell and a small flow of current (*Table 1*). The presence of zincs such as zinc oxide in a vulcanisate may perhaps add a little to a cells overall reactivity with an aluminium electrode and thus produce the small increase in the current seen here.

Crosslinking and Volume Resistivity (VR)

The current that can flow through a rubber component in an electrical cell when that rubber compound is fully vulcanised or cured and contains relatively large amounts of carbon black filler can be significant and is sufficient to lead to the ECD damaged material discussed here. The current can however be very much smaller than this in a compound again containing relatively large amounts of carbon black but with few crosslinks. Carbon black alone therefore does not provide a means for a significant flow of current and must be combined or linked together with a sufficient number of crosslinks before a current can readily flow through the material. Crosslink density can have a strong influence on the size of the current that may flow through a material and a fall in the crosslink density can produce an increase in the volume resistivity and a corresponding decrease in the current that may flow through the material. *Figure 11* shows the relationship between the current and the volume resistivity of an EPDM rubber containing 120 p.p.h.r. of carbon black. One of the compounds has a sulphur cure and the

other a dicumyl peroxide cure system. The compounds have been cured to differing degrees to achieve the various crosslink densities and thereby volume resistivity. A similar plot of the resistivity versus the current this time in a natural rubber based compound is also shown in *Figure 12*. A reasonably linear relationship is found between VR and the current in both the natural and EPDM based compounds and with both types of cure system. VR measurement could therefore be used in such a plot to help predict the current in a compound cured to different crosslink densities.

While ECD can create a porous and physically weak material, the degradation process does not normally continue indefinitely until the rubber has lost all of its integrity. The degradation process does appear to slow over time with the rubber reaching a weak but relatively stable condition. Any loss in crosslink density at the ECD sites would be expected to lead to an increase in resistivity and a corresponding fall in the current at the site. A fall in the current is likely to slow the degradation process and such a fall could account for the limited ECD seen. Other material sites with little ECD and lower resistivity will then be susceptible to the spread of further ECD.

While sulphur or carbon bonds themselves may not seem to be particularly suitable materials for increasing the electrical conductivity of a vulcanisate, their crosslinking of the rubbers network structure does appear to enable current flow in a material. If a crosslink bond can provide even a small degree of electrical conductivity the production of many and shorter pathways in the rubber network structure and between the rubber and filler particles by the crosslinking process could aid electron mobility through a material.

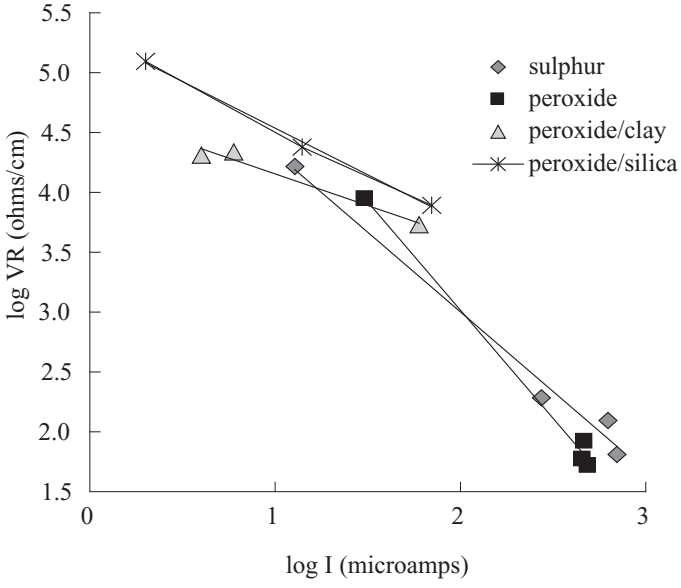

Figure 11. ECD current versus volume resistivity. The relationship between the current flow and the volume resistivity with EPDM vulcanisates with sulphur or peroxide cure and clay or silica filler.

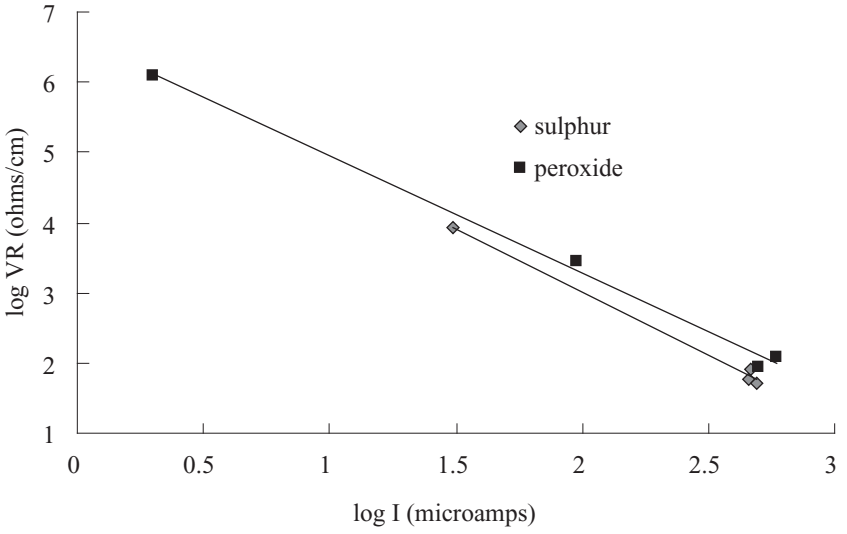

Figure 12. ECD current versus volume resistivity. The relationship between the current flow and the volume resistivity through natural rubber vulcanisates with sulphur or peroxide cure.

Filler and Resistivity

A rubber compound with a large carbon black content can be susceptible to ECD. To reduce this susceptibility to ECD additional fillers can be added or existing fillers replaced in a compound that increase the resistivity of the material. One option that can increase the resistivity is to add certain clays to a compound. Quite small loadings of clay added to a compound with a large carbon black content can be effective in raising the resistivity and improving ECD resistance while having little impact on the physical properties of a material. *Figure 11* shows the current versus resistivity of an EPDM peroxide cured compound containing 120 p.p.h.r. of N550 carbon black with and without 10 p.p.h.r. of clay. The clay has increased the resistivity and lowered the current in the material. The type of clay used in a compound can be important particularly with peroxide cured material. A clay with a nearly neutral pH value can be most suitable as the acidic level of some clays can disrupt the peroxide cure process leading to a fall in crosslink density and poorer physical properties although a fall in the crosslink density can improve ECD resistance. Silica filler was found to give no significant improvement to the compounds ECD resistance.

ECD Damage Analysis

While the physical form of the structural damage caused by ECD has been determined, the processes causing this structural damage are less well understood. The materials present in and around ECD damaged sites have been examined in order to further investigate the ECD process.

ECD damaged regions of a sulphur cured EPDM hose compound have been examined by SEM X-ray analysis. The X-ray scans have shown that zinc can be depleted at the centre of the ECD damaged sites to a level below that of the detection resolution of the instrument and zinc levels tend to increase moving away from these ECD damaged sites. The depleted zinc zones were found to encompass an area of some 10 to 15 millimetres around the ECD damaged sites. Zinc is an essential material for the maturation process in a sulphur cured rubber compound and any depletion of zinc is likely to inhibit further maturation or crosslink formation and perhaps lead to a lowering of the crosslink density.

Analysis of coolant liquid droplet exuded from ECD damaged regions of material has also found that these droplets can contain large amounts of sulphur. The presence of this sulphur implies free sulphur in and around the ECD damaged regions is likely to be depleted as well as the zinc.

A limited or fall in the crosslink density of the material because of the loss of zinc and free sulphur in a local region of the rubber compound is likely to make this region less able to resist any swelling taking place due to the ingress of liquid coolant. Large amounts of swelling have been found to occur at ECD damaged sites and the deterioration in the materials structure seen by the SEM at these sites does indicate a fall in the crosslink density of the material may have taken place. With a sufficient degree of swelling by the coolant further crosslink breakage can occur due to the swelling itself and such a loss of crosslinks can in turn lead to more coolant uptake and exacerbate the loss of structural strength of the material.

Peroxide cured vulcanisates typically show a greater resistance to ECD than sulphur cured material. A peroxide cured compound should not experience sulphur depletion or a loss of zinc and therefore any possible associated loss in crosslink density by ECD as these materials are not normally present and not necessary for the maturation process in these compounds. The absence of sulphur and zinc for maturation purposes and the reduction in the current flow also found in the absence of zinc in peroxide cured material may partially account for this materials better ECD resistance.

CONCLUSIONS

To limit ECD in hose for automotive cooling systems, a cooling system designed with non-conducting components between the hose and engine block that eliminates any current flow through the hose material is preferable. Where a current may flow through a rubber compound, the compound can be formulated with materials such as carbon black grades with a high volume resistivity, a peroxide cure system and certain clay fillers to inhibit ECD. An OAT coolant can also give improved ECD resistance. With a rubber compound exposed to ECD an economic balance may need to be found between replacing some of the materials such as low cost carbon blacks with more effective ECD resistant ingredients and any increase in the cost of these materials.

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