CHAPTER - I

GENERAL MODE OF DETERIORATION OF ELECTRONIC EQUIPMENTS & MATERIALS
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1.1 INTRODUCTION

1.1.1 In the case of electronic assembly a wide variety of materials are assembled into a single piece of equipment and generally crammed together in a small space out of necessity. A particular electronic assembly may contain several types of metals and alloys, different types of plastics and rubbers as insulators or dielectric; textiles, ceramics and paper etc as separators and insulators. The container may be of wood, plastics or leather. Inside the assembly, of course, there will be lots of greases, lubricants, varnishes and fungicides etc. Not only original materials deteriorate as such owing to the micro-climate inside the package, but in their process of deterioration they may influence the deterioration of other materials in the assembly [1].

1.1.2 Although beginning of electronics can be traced back to the Edison Effect (1883) and the invention of triode valve by Le-de-forest (1907), the real impetus to electronics came in, in the wake of development of transistor and its commercial exploitation about 4 decades back. The transistor performed the same function in the circuit as a valve. An analogy showed that, the transistor had a cathode (emitter), a plate (collector) and a modulating grid (base). Thus the transistor.
was regarded as a micro-miniature valve, operating at lower power levels and with greater reliability. It still acted as an amplifier or switch, and more important, resistors still looked like resistors and capacitors like capacitors.

1.1.3 A new era has since dawned and instead of discrete components, integrated circuits are coming into vogue. There is an apparent change in that, although the applied voltages are low, the field intensity in capacitors and other films are very high on account of their thinness. The failure rates on account of environmental changes are therefore likely to increase unless these are properly protected.

1.1.4 This is the era of micro-electronics. No longer are resistors and capacitors as easy to recognize. These passive elements along with the active devices may form an integral part of a SILICON-CHIP. The transition from transistors to chips, has brought in its wake, many problems connected with the environment. Semi-conductor materials used in electronic devices are nearly perfect single crystals, although amorphous semi-conductors are fast gaining ground. The presence of a very low concentration of chemical defects (impurity atoms), and structural defects (dislocations, vacancies etc) can produce an environment which may have pronounced effect on their properties [2].

1.1.5 Failures of electronic equipments and assemblies in extremely adverse climates of certain major theatres of the
second World War eg. Burma-infested with biological agents and having high degree of humidity, Sahara-Desert-having a wide variation of temperature between day and night coupled with low humidity and dust laden atmosphere, coastal areas-dripping with moisture and the snow covered areas having temperatures as low as -40°C, focussed the attention of the workers on the deterioration of electronic equipments owing to varied climates. The earliest report on climatic deterioration of electronic equipment is from the Australian Army Mission to New Guinea in 1943, where electronic equipment dumped in packing cases by the Australian Army completely failed. US Army Air Force Tropical Sciences Mission in 1946, likewise, reported numerous examples of failure of electronic equipment in many parts of the world [3]. They ascribed it to the Corrosion of metallic and non-metallic components due to adverse environmental conditions. Example of deterioration due to extreme environmental conditions are cited in many defence documents. Subsequently, a lot of work has been done to standardise the electronic equipment especially for the services and a rigid testing schedule evolved.

1.2 EFFECT OF CLIMATIC ENVIRONMENTAL FACTORS

1.2.1 Electronic equipments comprise materials and goods processed from various naturally occurring (organic, inorganic) and synthetic substances which are susceptible to deterioration under different climatic and environmental
conditions. The deterioration of equipment will depend to a great deal on ambient temperature, moisture, atmospheric pollution, air-borne dust, ultraviolet light, radioactive radiations, biological and entomological activities [4]. Normally, temperature variation alone constitutes a great hazard to electronic components, yet this bears no relation to actual conditions in which the equipment has to live and breathe[5]. Extremes of climate that an equipment is required to withstand can be categorized as follows:-

(a) Tropical climate - Wherein high temperature is combined with high humidity.
(b) Desert climate - Where atmospheric humidity is very low but diurnal variation of temperature is very wide.
(c) Arctic conditions - Where very low temperatures are in operation for long periods of the year.

1.3 TROPICAL WET CLIMATE

1.3.1 Large areas of India are tropical wet climate. In such areas there is no month with an average temperature lower than 17.8°C. Average temperatures are more typically around 26.7°C - 27°C, relative humidity is usually high and rainfall is abundant. It is never less than 30 inch an year and often exceeds 100 inch. Dew points are high, which means that a small drop in temperature is sufficient to produce 100% rh. This type of climate is conducive to metallic as well as microbial corrosion. At 95 - 100% rh, an optimum temperature of 30°C produces fungal growth in susceptible materials. Relative
humidity plays an important part both for metallic corrosion as well as fungal growth. Below 70% rh fungal growth is negligible [6]. All organic materials are liable to deteriorate due to the presence of moisture and nutrients causing fungal growth. Metals will corrode more rapidly and electrolytic action between dissimilar metals is considerably accelerated [7].

1.3.2 Moisture is absorbed by insulating materials, resulting in the lowering of surface and volume resistivity. Also an increase in the absorbed water leads to swelling of materials and electrical and mechanical breakdown can occur.[8]

1.3.3 The presence of mould or fungi can be destructive to electrical and electronic devices and equipment, due to the metabolic process associated with growth, which causes etching to take place on the surface of materials. In addition the fungal growth forms a low resistance path [9].

1.4 DESERT CLIMATE

1.4.1 In desert conditions, high ambient temperature, combined with heat dissipated by the devices, can produce internal temperatures well over 110 C. Because of very low moisture content in deserts, plastics warp, certain materials lose tensile strength and materials embodying paper disintegrate[5].
1.5 ARCTIC CLIMATE

1.5.1 In arctic conditions embrittlement and cracking of the materials can occur both in metallic and non-metallic materials [4]. Sealing properties can be ruined due to shrinkage and cracking. Occurrence of whiskers in tin-plated finishes is a common phenomena. This may even lead to bridging of the conductors thereby causing an electrical breakdown[10].

1.6 THE PLASTIC ENVIRONMENT

1.6.1 Much of the progress towards ever greater miniaturisation made by the electronics industry, from the very days of valves to the development of the transistor and later the integrated circuit has only been made possible because of the availability of polymeric materials. Indeed, many new plastics have been developed specially for electrical and electronic device applications and as a consequence the plastics and electronics industry have continued to grow side by side.

1.6.2 Much of the driving force behind the development of many modern plastic materials came from the electrical and electronic industries, largely because of the numerous areas for application in electrical and electronic components. Today, plastic materials are widely used through all areas of electrical and electronic device production in diverse applications ranging from alpha particle barriers on memory
devices to insulator mouldings for the bushings and transformers.

1.6.3 Plastics, or more correctly polymers, find use as packaging materials for individual microcircuits, protective coatings, wire and cable insulators, printed circuit boards, components, die attach adhesives, equipment casings and a host of other applications.

1.6.4 A typical radio manufactured 30 years ago would certainly have a case made from a dark brown 'bakelite' type phenolic resin and inside this would be components covered in a variety of strong smelling sticky waxes or bituminous materials. Since then, steady improvements in plastic technology have paved the way for a huge selection of materials to be manufactured that are used in electronics applications, unimaginable in the 1950s. Today plastics are used throughout all sorts of applications in the electronic industry right from the manufacturing processes to the final packaging as well as in the individual microcircuits themselves.

1.6.5 Polymeric materials are used as the basic photoresists for making metal patterns on printed circuit boards, and also on the individual integrated circuit devices themselves. The circuit boards are made of various glassfibre filled epoxides and polyesters, and are usually coated with other polymeric materials to prevent tarnishing and to improve solderability.
The devices that are mounted on the completed printed circuit boards may have been manufactured using polymeric photoresists and have plastics such as polypropylene and polyester films in capacitors or epoxide resins in integrated circuits and transistors. The completed boards containing various devices are often then coated with another protective polymer.

1.6.6 Polymers have come to stay as the main plank of electronic industry. The deterioration of polymers under normal use conditions is a major factor limiting application of these remarkable and versatile materials. As the chemical reactions responsible for degradation proceed, the properties of the polymers are affected adversely. Loss in mechanical strength, dielectric properties, insulation resistance, and aesthetic look result in failure of the polymer. Changes in mechanical properties result from reactions which either reduce the size of molecules or lead to crosslinking between polymer chains to form rigid three dimensional structures[11]. On the other hand changes in electrical properties occur when polar groups accumulate in polymer molecules. These latter reactions may occur either along the backbone chain or at side groups with little change in molecular weight [12]. Natural rubber is well known to degrade by absorption of oxygen and also on account of ultraviolet, ozone and ionising radiations.

1.6.7 Ionisable impurities in a plastic become mobile in the
presence of moisture particularly at high temperatures. These impurities tend to move to the chip surface and may cause junction inversion, an increase in leakage current under reverse voltage and also corrosion of metallic interconnections [12].

1.6.8 A great deal of research work has gone into the study of degradation of polymers and its stabilisation on account of heat alone, thermal oxidation, ultraviolet and other ionising radiations but a detailed study of the polymers on account of the exhalations emitted by it during the normal course of use for example in a confined space has been lacking.

1.7 CORROSION OF METALS BY PLASTICS

1.7.1 Corrosion of metals by vapours given out by organic materials has been investigated by Rance and Cole [13] Knotkova Germakova and Vlckova [14] and by Donavan and stringer [15,16]. These papers deal largely with the effects of vapours from plastics in an undegraded (freshly manufactured) condition; additionally Knotkova Germakova and Vlckova [14] refer to corrosion arising during manufacture. The vapours arising from thermal degradation of plastics has been reported by kennet[17]. Cotton and Jacob[18] have talked of corrosion from vapours of PVC and from fluorinated polymers. Phenolic resin mouldings may evolve ammonia which corrode brass, ni or silver. Flux residues,chemicals added to plastics as accelerators,stabilizers etc create an atmosphere
for metallic corrosion in confined spaces [5]. Corrosion has also been caused by acids produced out of microbiological decompositions [19]. Clark and Longhurst[20] have shown that corrosion in air containing acetic acid was very slow below 70% rh and increased tremendously beyond 80% rh. The exhalates evolved by plastics are summarised in table 1.1 [21].

1.8 CORROSIVE EFFECTS OF TIMBERS ON METALS UNDER HOT HUMID CONDITION.

1.8.1 It is well known that severe corrosion of metal occurs when the humidity exceeds 80% rh [20]. Corrosion is also generally augmented by the presence of organic acid vapours. The corrosion of metallic equipment enclosed in wooden boxes stored under certain climatic conditions have been reported by several workers [22-32]. The cause has been attributed to the evolution of volatile organic acid vapours from wood under these conditions. It has been generally established that the free acid vapours are derived by mild and progressive hydrolysis of the acetyl group attached to hemicellulose in wood [33,34]. The acetyl content of wood hemicellulose differs from species to species as also from timber to timber within a species [22,23]. However, irrespective of the acetyl content wood may serve as a source of acetic acid when stored under hot humid conditions. Although the rate of hydrolysis of the acetyl hemicellulose will vary from species to species, the risk of corrosion to metallic equipment in closed wooden boxes under hot humid conditions is difficult to avoid.
1.8.2 It may not be possible to make any arbitrary classification of wood as safe and dangerous because it would entirely depend upon the environmental conditions to which they are subjected and the relative susceptibility of metals towards different species. Corrosion induced by coir fibres in packaging has been studied by Sanyal et al [35]. The extent of damage which can be caused by organic acids emitted out by paints, varnishes, wooden cases, insulating and cushioning materials has been reported by various workers and some remedial measures by way of volatile corrosion inhibitors suggested [36-41].

1.9 EFFECT OF TEMPERATURE ON ELECTRONIC EQUIPMENT FAILURE

1.9.1 Extremes of temperature are often responsible for the failure of equipments & components. During hot season, a number of adverse consequences have been reported in operating the equipments at high temperatures. The temperatures reach values where some of the materials start melting eg. greases, protective compounds and waxes become soft enough to flow. The heat distortion temperature of most thermoplastics is below 95 C. and the deterioration of cellulose insulation begins at about 37.8 C. Differential expansion of separate elements result in the distortion of assemblies, the rupture of seals, and the binding of movable parts. Long range ageing processes are accelerated at high temperatures, organic materials decompose more rapidly and rubber materials harden and set. [3,5,7].
1.9.2 At extremely low temperature say -40°C, many components cease to function on account of the physical changes that occur within them. Electrolytic capacitors become completely unsuitable and quartz crystals fail to oscillate because of mechanical changes. Storage battery electrolytes solidify, ordinary lubricants harden and those in the rotating shafts, gears and bearings of equipments may freeze. Waxes and protective compounds stiffen and crack. Rubber components lose their flexibility and become brittle. The variation in the capacitance, inductance and resistance of component parts, with changes in temp. may be so great as to require readjustment in critical circuits.[3,5]

1.10 EFFECT OF MOISTURE ON ELECTRONIC EQUIPMENT FAILURE

1.10.1 One of the most serious problems faced in World War II was the deterioration of electronic equipments by moisture in humid regions. Moisture altered the electrical constants of tuned circuits causing loss in sensitivity of the signal equipments, it damaged the components and insulation, it promoted the corrosion of metals and favoured fungal growth [5].

1.10.2 The most important factor that will degrade the performance of an electronic equipment and deteriorate the capability of materials and finishes is moisture. Table 1.2 shows the various related moisture factors that can affect the performance capability and service life of electronics. The
first column lists the forms in which moisture will occur. Except for condensation, moisture can be invisible until an excess of moisture accumulate in poorly sealed containers. The second column in the table lists the types of changes in the circuit, part, material performance that will be noticed in degradation or catastrophic failure. The third column lists those rate factors that will increase the deteriorating effect of moisture. Moisture itself is a rate factor for most deteriorating effects, and therefore, dry condition of operation is the safest protection [5].

1.10.3 The amount of moisture present on the surface of the dielectric depends upon the nature of the surface and relative humidity. If the relative humidity is high, surface becomes wet easily. Wax, polystyrene, silicones etc. prevent the formation of continuous film of moisture whereas quartz, glass and the steatite porcelains wet easily [42].

1.10.4 Moisture degrades insulation by first wetting its surface and reducing the surface resistivity. The rate of moisture absorption into the insulation depends upon the water content of the surrounding atmosphere, the water vapour transmission rate of the surface of the material and the hygroscopicity of the material. 70% is the critical humidity for corrosion of metals [42].

1.10.5 There is a wide difference between dielectric
constant of water and most of the insulating materials. The water content on the surface and within the dielectric increases the capacitance and also the dissipation factor. Heat dissipation [8] ultimately leads to the thermal breakdown of the material. When the atmosphere is extremely humid, condensation of moisture within the equipment during cool night takes place and in the case of aircraft electronic equipment, the decrease of temperature rapidly with altitude may also result in condensation [42].

1.10.6 Heavy deposits of moisture on surfaces greatly increase the moisture absorption of vulnerable materials. Electrical discharge between high tension points is more likely to occur during periods of condensation under the intermediate insulation if of a nonwetting type [43].

1.10.7 Breathing is another type of damage flourishing under humid conditions. Here water gets accumulated in partially sealed containers. The air in these containers becomes warm during the day and portion of it is expelled as the pressure increases. At nights when the temperature drops, air flows back. Further lowering of the temperature causes condensation with the result that there is a net increase of moisture in the container with each cycle. Hence in design of electrical & electronic components primary consideration should be given to the provision of ventilation [44].
1.11 EFFECT OF ATMOSPHERIC PRESSURE ON DETERIORATION OF EQUIPMENT

1.11.1 Some electrical components fail at high altitudes. Amongst these are the plugs in electrical connectors in which voltage leakage occurs between the pins and the shell across the surface of the insulating material. Vibrator and relay contacts are damaged more rapidly at reduced pressure since the intensity of the electric arc increases upon making and breaking the contact [42].

1.11.2 Even though complete electrical breakdown does not take place over an insulating member, an electric discharge consisting of minute arcs may occur at metal points or projections where strong electric fields are built up so that the surrounding air is ionised [7]. Ionisation of the air produces ozone and oxides of nitrogen, which are undesirable. Ozone oxidizes natural rubber and some synthetic formulations and the oxides of nitrogen combine with water to give acids which contaminate and degrade insulators, bushings and severely corrode metals [5,7].

1.11.3 Rapid changes in both temperature and atmospheric pressure can cause distortion of seals and such changes are frequently responsible for entrance of moisture into gasketed containers [5].
1.12 CONTACT CORROSION IN ELECTRONIC PACKAGING

1.12.1 It is known that even clean metal surfaces are covered by insulating barriers. When two contact surfaces are pressed together these barriers are broken at a number of discrete 'Contact points' and therefore, relatively high current density flows at these points [5]. Studies made by various researchers suggest that the area through which the current flows may be less than one millionth of the total contact. Actual contact surface being limited to minute pin holes and cracks in the insulating barriers, it is easy to see how the surface conductivity and the current flow are affected by changing stresses, fluctuations of temperature and pressure and particularly by continuous growth of barriers. These barriers can be either harder or softer than the metal itself depending upon the mode of corrosion [5].

1.12.2 Not only do oxide or organic films increase contact resistance, they also lead to increase in volta or contact potentials to levels higher than the theoretical value. For example a monolayer of adsorbed oxygen on a tungsten surface will increase the work function and hence the contact potential, by an order of volts [5]. Although these very low potentials can normally be ignored, they can affect the performance of devices in low stress environments; these are still present even when equipment is switched off or in storage, and can accelerate degradation by galvanic action. Contact resistance is an important parameter of many types of
devices, some of the more significant being resistors, connectors, potentiometers, switches and relays.\[45\]

1.12.3 Although less widely reported than the effects of vapours, contact corrosion has been a serious problem in packaging and in electronics [44-47]. As miniaturisation and sophistication of electronic devices has increased, the hazard presented by corrosion is often the limiting factor inhibiting the attainment of expected levels of reliability. Semiconducting devices, switches and miniaturised v.h.f circuits are all particularly sensitive to the slightest reaction on critical surfaces, and in devices calling for the highest levels of reliability even the most inert of the phenolic, epoxide and silicone resins are not considered to be fully acceptable [48,49]. Corrosion of electronic assemblies may often be enhanced by migration of ions to sensitive areas under applied potentials, and by local heating effects associated with current flows. Some work in this direction has been done by Czechoslavakian workers[14]. In general plastics that give rise to vapour corrosion will also cause contact corrosion. A paint may give rise to corrosion of the adjacent metal items, while protecting the metal substrate on which it is applied. Access of the air and water will also affect the corrosion rate. Metal inserts in corrosive plastics are most actively attacked at the plastic\metal\air interfaces [50].

1.12.4 With certain metals notably Al, Titanium [51] and stainless steel, crevice effects (Oxygen shielding and
entrapment or water) frequently accelerate attack. Acceleration of corrosion by bimetallic couples between carbon fibre reinforced plastics and metals presents a problem in the use of these composites. The chloride ion is the most frequent cause of contact corrosion, since chlorine is present in the many chlorinated plastics, and is also frequently retained in residual amounts from reactive intermediates used in manufacture. Thus epoxides usually contain chloride derived from the epichlorohydrin. In addition to the contaminants referred to in the table-1.1 various metal and ammonium cations, inorganic anions and long chain fatty acids (present as stabilisers, release agents derived from plasticisers) may corrode metal on contact [52,53,54].

1.13 WHISKER GROWTH CORROSION IN ELECTRONIC EQUIPMENT

1.13.1 Corrosion is chemical interaction between a metal and its environment. Electronic components invariably contain metals of one sort or another and as such suffer corrosion with effects that may range from slight tarnish to a considerable incrustation of corrosion product and consequent metal loss [53]. Whisker growth is another spontaneous metal surface phenomenon which can cause trouble in electrical equipment. The growth of whiskers was recognised over 25 years back as a constant source of trouble in electrical/electronic equipment. The susceptible metals are generally Cd and Zn, more so when they are in the form of thin electrodeposits—a form in which they are generally used as a protective measure
against the corrosion of inside metals [48]. Thin coatings are more likely to give trouble than thick ones, but thick coatings do not offer absolute resistance against whisker growth [55].

1.13.2 Whiskers are metal single crystal filaments, about 10,000 \( \text{Å} \) in diameter. Their lengths depend upon the neighbourhood metals or substrate [53]. The growth mechanism is not yet precisely known but the energy for their formation seems to be owing its origin to the release of micro-stresses in the metal. Many metal and environmental factors affect whisker growth, but only to a certain degree; with Tin coatings for instance, growth is favoured by high ambient temperature and humidity, although whiskers have been grown at below 0 deg C and also in evacuated containers [10]. Applied pressure generally accelerates growth. No universally applicable protective measures are known. The whiskers grow under practically all conditions from vacuum to highly corrosive humid environments. Recent investigations have shown that the presence of small amounts of lead in excess of 1% in electrodeposited tin results in a marked decrease in whisker growth [55, 56].

1.13.3 Whisker growth is an important consideration in design, especially where components coated with \( \text{Cd}, \text{Zn} \) may be placed in proximity to each other, whiskers can bridge this gap. They are at times capable of carrying currents as high as 25 mA, without being burned off [53]. The problem of whisker
growth is more serious with tin because it is used extensively as a coating where soldered or wirewrapped connections are used. The distance between terminals used for soldered or wirewrapped connections is usually quite small resulting in more instances of difficulties due to whisker growth. Because of this the use of pure electro deposited tin should be avoided, especially in lowvoltage electrical equipment where relatively narrow spacing exists between parts which must remain electrically isolated.[53,57,5R]

1.13.4 Cadmium as a protective coating metal behaves much like Zn. In most atmospheric environments Cd is usually electronegative to iron and protects exposed areas of iron by the same sacrificial action as Zn. Cd coatings are superior to Zinc in marine locations and locations other than industrial atmospheres. In tropical marine exposure, Cd is corroded more severely than in the similar locations in temperate zone. This is somewhat contrary to the behaviour of Zinc. Cd behaves better than zinc in humid environments where condensation occurs. Under these conditions, Cd will tarnish, sometimes turning quite dark, perhaps due to incidental sulphur contamination from the atmosphere. Unlike Zinc, Cd will not develop voluminous white corrosion products. When chromated, an even better behaviour can be expected under these conditions. In stagnant air particularly in the presence of organic vapours that may emanate from plastics and from paints, white to yellowish deposits will form on Cd surfaces. These may be minimised by a chromate treatment[53].
1.13.5 Faults due to the growth of Cd, tin and zinc whiskers on a wide variety of electronic devices have been found; these are due to low impedance bridging between closely adjacent parts of low voltage circuits,[5] for instance between the plates of metal rectifiers, the lugs of connecting strips and relay members. Trouble can also arise from whisker growth on purely structural members such as chassis and covers if the filaments are subsequently dislodged and fall across sensitive circuit elements. The importance is more so now in view of greater emphasis on compactness and miniaturisation [5].

1.14 METAL MIGRATION CAUSED COMPONENT FAILURES

1.14.1 Silver is used to some extent in electrical contacts. It has excellent corrosion resistance in most environments. However, it reacts rapidly with sulphur containing atmospheres, even at low humidities. This can be prevented or minimised by applying an extremely thin layer of electrodeposited rhodium [59].

1.14.2 One drawback of silver is that it has a tendency to migrate under the influence of an applied potential in the presence of high humidity, forming filamentary or dendritic structures[5]. Growth requires the presence of a potential between two electrodes of which at least the anode is a silver metal, separated by an insulating material. The silver anode corrodes, and the highly mobile silver ions migrate to the cathode where they are reduced to metallic silver [45, 53].
1.14.3 Insulation moulding of the phenol formaldehyde type are well known to promote this type of failure, especially if they contain cellulosic fibres. Silver ions migrate from the anode over the surface of and very occasionally through, the dielectric and either become deposited as metal on the cathode, giving tree-like growths or by virtue of reducing substances present in the insulant are converted to the metallic state at intermediate points. When the insulation resistance has become sufficiently reduced, failure ensues by arcing and tracking [59]. Silver seems to be unique in this behaviour and its use has had to be abandoned for many purposes. Use of silver with any insulating material except Mica is basically considered a bad practice [5].

1.14.4 Zinc is also known to migrate. Copper is used as undercoating to prevent zinc migration through solder, tin and gold. Copper is also employed as masking coating in case-hardening, when it is desirable to prevent hardening of certain areas of a component part[53].

1.14.5 Metal migration, it has been suggested, consists in the formation of an unstable hydroxide of metal on a surface that has adsorbed moisture, followed by the diffusion of hydroxide and its reduction back to the base metal in another location with formation of METAL DENTRITES that ultimately cause failure [58]

1.14.6 CP Lascaro cites the case of failure of a ceramic
capacitor due to the use of silver contacts with a migrated silver path over the ceramic insulation which was wettable and had a direct current polarization potential present. In time the silver migrated over the ceramic insulation to create a shunting path. Since silver has a tendency to migrate under such condition, prevention is effected by substituting silver with another less vulnerable contact metal [60].

1.15 MICROBIOLOGICAL GROWTH IN ELECTRONIC EQUIPMENTS

1.15.1 Continuous high temperature and humidity prevailing in the tropical forest regions provide the most favourable conditions for activity of micro-organisms which bring about deterioration of electrical equipments[7].

1.15.2 Microbiological deterioration involves damage to materials which render them unsuitable for intended use or reduce their useful life or diminish their desirable properties. The deterioration may be ascribed directly to micro-organisms, which utilise part of the structure as food material or indirectly to them when the products produced and the environments created by micro-organisms have a corrosive effect. The main types of deterioration includes surface-colonies, discolouration, decomposition with loss of strength or change of chemical, physical or mechanical properties and the production of toxic substances.[7]
1.15.3 For micro-organisms to develop in or on a substrate there must be sufficient nutrients present, adequate moisture, and suitable temperature for growth. Factors such as oxygen concentration and degree of acidity influence the type of organisms which develop. Fungi which are commonly occurring on the electronic equipments in the tropical areas are: Aspergillus niger, Aspergillus flavus, chaetomium globosum, Pencillium, Trichoderma sp, Murcor sp, Monilia sp, Rhizopus nigricans, Actinomycetes [4]. Aspergillus niger, chaetomium globosum and a netaraizium have been used as test organisms for testing fungal resistance of air borne electronic equipments [7]. Aspergillus chevalieri has been found growing on plastic terminal blocks of electrical installations in the Panama canal zone in almost pure culture form [7].

1.15.4 Greathouse and Wessel (1954) have mentioned that during world War II in the tropical jungle regions the electronic equipments were covered with a net-work of fungi. The extent of fungus growth in equipments has often been considered to be a measure of the extent of deterioration.

1.15.5 Insulating materials which contain cellulosic derivatives are most susceptible to fungal attacks. Moisture infiltrates through electrical insulation resulting in fungal growth. Although the climatic conditions in the tropics are most favourable to the life process of fungi, the colder middle latitude also support fungal growth if the humidity is high [7].
1.15.6 Leutritz and Herman[61] studied the effect of high humidity and fungal growth on unfilled and inorganic filled plastics by exposing the specimens, inoculated with fungi to 97% rh. The insulation resistance of the specimens dropped from initial values of between 3,500 and 1,000,000 megaohms to below 1,000 megaohms within a period of 1.5 hours. The authors concluded that the materials made from organic and inorganic filled plastics may be so rapidly affected by water absorption that any adverse effect by fungal growth is negligible.

1.15.7 Witt [9] studied the effect of moisture and fungi on the mechanical and electrical properties of a few selected plastic materials by exposing samples to high humidity. Profuse growth of fungi was observed only on cotton fabric reinforced phenolic laminates. On exposure of the sample of insulators to natural surroundings in tropical test stations, Wasserbauer(1967) found that the samples were generally attacked intensively only for certain critical periods during which optimal conditions exist for growth of moulds. The critical periods last for atleast three consecutive days at a continuous rh in excess of 90% with a daily rh minimum greater than 75% and lowest daily temperature of 15 C.

1.15.8 According to Wasserbauer (1967) the degree of microbiological corrosion of electrical gear exposed in humid tropics depends primarily on the number of spores in the surroundings and their activities with respect to the substrates. Both of the above factors are affected in part by
climatic conditions, mainly relative humidity and temperature. The activity of spores depends further on operating conditions and the duty cycle of the electric gear.

1.16 ATMOSPHERIC CORROSION OF METALS

1.16.1 Colossal losses are known to occur due to corrosion of engineering and construction materials on account of their exposure to environment. In 1949, Uhlig[62] estimated 5500 million dollars as the annual loss in USA. Vernon calculated that 600 million pounds were annually spent in corrosion control in U.K.[63] in the fifties. Rajgopalan puts this figure in India at about 150 crores in 1960-61 [64].

1.16.2 The main gaseous impurities commonly found in atmosphere are SO2, NH3, H2S & HCl. In addition to these there are gases such as CS2, NOx and Cl2 which are the common effluents from industrial and chemical works. Other materials which have been found include aldehydes, vanadium compounds, SO3, H2SO4 and CO [65].

1.16.3 The most important corrosive constituent of industrial atmosphere is SO2, which originates from the burning of coal, oil and gasoline. In certain industrial climates like that of New-York it may vary from 0.06 to 0.25 ppm. It is estimated that in New-York approximately 1.5 million tonnes of SO2 are generated by the industries per year. SO2 content at various sites in India has been determined [66] using lead peroxide
candles in louvered boxes. It has been found that a concentration of 0.25 p.p.m SO$_2$ in the atmosphere results in the deposition of 1 mg. per sq dm. per day of SO$_3$ [67,68]. SO$_2$ in atmosphere varies with season, being higher in winter due to higher fuel consumption.

1.16.4 It has been estimated that the average time SO$_2$ remains in the air is 12 hours. About one fifth of this is brought down by falling rain and a similar amount is blown out to sea. Much of the remainder is retained on structures or vegetation [69].

1.16.5 Generally concentration of SO$_3$ is estimated to be about one hundredth that of SO$_2$ [70]. The role of SO$_3$ in the atmosphere is of importance as it raises the dew point of air containing SO$_2$ so that condensation occurs on metal surfaces more easily and at higher temperatures.

1.16.6 Oxides of nitrogen are probably formed by electrical discharge in the atmosphere and to a small extent by the oxidation of ammonia. These oxides unite with water to form nitric acid. The nitric acid has been reported in the atmospheres of tropical regions but, generally the nitric acid is combined with ammonia. Nitric acid is washed down by rain and it has been estimated that no less than 25,000 tons of nitric acid are produced in 24 hours but only a small amount of this is washed down by rain and falls on soil. About 3 lbs.
of ammoniacal nitrogen and 1 lb. of nitric acid is returned on earth per acre per annum. During the dry weather, accompanied by very little rain, 1 part of oxides of nitrogen in 4 or 5 million parts of air has been found. At the same location, different amounts of nitric acid (0.3mg to 1.0mg) in rain have been reported in different seasons. Parker[71] has stated that 140,000 tons of nitrogen oxides are emitted annually at ground level from petrol driven vehicles.

1.16.7 Some coals have a comparatively large chlorine content (about 0.75%) probably present as inorganic chlorides[72]. The content of F is about 0.1% and it is given off as hydrogen fluoride and silicon tetrafluoride. A small quantity of ammonia is given off by the combustion of coal, this being the main source of ammonia in the atmosphere, although the decomposition of organic matter makes its contribution. Normally the ammonia concentration in the air is 0.008 ppm.

1.17 ACTION OF CORROSIVE GASES ON METALS

1.17.1 Lessing [73] has discussed the part played by ash and other suspended particles as carriers for sulphur compounds. When a solid particle is in collision with pre-existing SO₃ or H₂SO₄, a hygroscopic film is formed on it, which can then collect SO₂ after deposition on a metallic surface. Such acid-coated particles may cause much corrosion to metals. Barton [74-75] has shown that dusts with water soluble constituents, especially chlorides and sulphates, set up corrosion centres on
steel, which spreads slowly. Preston & Sanyal [111] and Sanyal & Badhawar [115] have discussed the role of nuclei in atmospheric corrosion.

1.17.2 Hudson and Stanners [76] found a direct relationship between the SO2 pollution and the observed rates of corrosion of steel and zinc exposed at several sites in U.K.

1.17.3 The importance of ammonium compounds has been emphasized by Harrison and Tickle [77]. Their findings apply in part to painted surfaces. They point out that other factors besides SO2 seem to be operative in deciding the corrosion rate; at Billingham the corrosion proceeds faster than the SO2 content would predict, whilst with a three fold increase at Derby there is no increase in the corrosion rate. They provide interesting information about the ammonium salts found on steel at different locations.

1.17.4 Sereda [78-81] has established that measurement of temperature, SO2, and time of wetness of metal surface yield data from which systematic evaluation of atmospheric corrosion of steel is possible.

1.18 EFFECT OF SUSPENDED & SOLID CONTAMINANTS ON METALS

1.18.1 In indoor exposures, Vernon [82] found that rusting could be entirely suppressed by screening steel specimens within a muslin cage or by filtering the air so that contact
of metal with solid suspended particles in the atmosphere was avoided. The unscreened specimens rusted freely. Sanyal et al [83] exposed metal specimens inside circular cages made of wire meshes of different apertures and showed that the rate of corrosion was directly proportional to the amount of particles entering the cages and depositing on the metal surface. Mild steel and zinc were less corroded inside cages made of fine wire mesh; the quantity of dust was also lower.

1.19 EFFECT OF CONDENSATION AND MOISTURE ON METALS

1.19.1 At atmospheric temperatures, the metals used in engineering are generally resistant to direct oxidation and suffer rapid attack only when electrochemical action take place. Usually an electrolyte is provided by a film or pocket of condensed moisture on metal surface or by wetting due to exposure to rain.

1.19.2 On exposure to air, almost all metals become covered with a surface film of oxide. Such films are very thin (about 100 Å) and firmly adherent. They occupy substantially the whole volume of the metal and are protective [65]. In dry air the metal remains uncorroded. However, where the metal is exposed to damp atmosphere, the metal surface is liable to acquire a film of natural water, so that the immediate environment is, instead of dry air, an electrolyte solution. Under such conditions a thin air-formed film generally affords little protection. Although it may be impervious to molecular
1.19.3 The factors affecting atmospheric corrosion are numerous. The more dominant factors are humidity, precipitation, fluctuation of temperature, time of wetness, wind direction and wind-velocity, solid particles and gaseous impurities present in the atmosphere. To understand its mechanism properly, it is imperative to study the corrosion behaviour of metals under controlled laboratory conditions. As a result extensive laboratory work has been carried out by various workers [84-104] on atmospheric corrosion of metals under different conditions.

1.20 LABORATORY STUDIES OF ATMOSPHERIC CORROSION

1.20.1 Vernon [105-108] established the important principle of critical humidity for corrosion. Only when the relative humidity of the atmosphere exceeds a certain critical value, corrosion becomes important. Below the critical there is no corrosion, although an air formed oxide film grows which shows some weight increase of specimens. Above critical humidity certain hygroscopic substances present on the surface of metal or formed during the attack are able to absorb water from the atmosphere and corrosion continues by a mechanism met with water immersed condition. The critical value of relative humidity above which corrosion of iron becomes rapid is about 70%.
1.20.2 Vernon [108] has shown, in laboratory experiments, that in purified air of high relative humidity, the rusting of mild steel is greatly reduced owing to the strengthening of the primary film at early stages, if the higher humidities are approached gradually from zero; the metal remains bright in the early stages. At approximately 50% rh. (the primary critical humidity) there is pronounced increase in the rate of attack and the specimen becomes rapidly covered with rust. The primary critical humidity marks the requisite relationship between water vapour, oxygen and SO₂ for rusting to commence. The secondary critical humidity depends only on the properties of the initially formed rust, probably associated with its gel structure and is independent of the presence of SO₂.

1.20.3 Sanyal and Badhwar [104] observed that each metal requires a minimum humidity for the initiation of corrosion. The critical humidities at which the rate of corrosion is accelerated in the case of iron and aluminium, have been found to be 60% to 75% and 80% respectively. Copper and zinc do not exhibit any critical humidity.

1.20.4 The rate of atmospheric corrosion is determined by the simultaneous action of the critical relative humidity exceeding a minimum value and of the aggressive gases and vapours. This has been reported by various workers [76, 108, 109].
1.20.5 It was shown [85, 110, 111] that only in the range above the critical humidity, an adsorbed water layer is present on the metal surface which has the capacity to absorb aggressive gases from the atmosphere and to act as an electrolyte during the electrochemical process.

1.20.6 The role of contaminants in atmospheric corrosion has been studied by Sanyal and Preston [114] & Sanyal and Badhwar [115]. Corrosion has been found to increase with increase in humidity, temperatures, period of exposure and concentration of electrolyte. It is also influenced by the pH of the solution used for inoculating the metal surface.

1.20.7 Evans [111] carried out a series of experiments with different metals exposed over H2SO4, HCl, H2S, SO2 & CO2. The corrosion of metals varied in both intensity and nature. The hygroscopicity of corrosion product formed in each case determined the nature and extent of corrosion. Corrosion was absent or minor over H2SO4, water or CO2.

1.20.8 Hydrogen sulphide discoloured most of the metals, SO2 produced maximum attack on metal and formed hygroscopic corrosion products in the case of iron, zinc and nickel. HCl vapours attacked zinc and iron forming soluble corrosion products. Over ammonia, Copper and brass were attacked. One feature of all tests is that in cases where the specimens become damp and wet, there was rapid attack. There was very little corrosion over water and CO2. The corrosion of vapours
from organic materials have been reported by several workers
[112,113,20-23]. Clarke and Longhurst [20] have shown that
very small amounts of acetic acid (0.5 ppm or less) can
promote corrosion at 80% rh and above, their results place
acetic acid in the same dangerous category as sulphur dioxide.

1.21 THEORETICAL PREDICTION OF LIFE OF MATERIAL

1.21.1 The Electrical Engineering Research Institute, Prague
at the request of the Czechoslovak industry, established a
special department for research into the way various climatic
factors and service stresses affect the ageing of electrical
equipment. A large number of outdoor exposure stations were
setup where a wide range of materials and components were
subjected to exposure tests and later evaluated. The
information thus obtained yielded a good deal of insight into
the mechanisms and kinetics of the degradation processes
involved. Computer processing of the amassed data has yielded
a set of climatic maps and research procedures for predicting
the probable extent of degradation caused by exposures at
various locations. Theoretical predictions of the life of
various electrical grade materials, taking into account the
climatic conditions at various locations in India have been
presented in the form of maps. (figs 1.3, 1.4, and 1.5).
### TABLE 1.1

<table>
<thead>
<tr>
<th>Material</th>
<th>Volatiles evolved (on heating or hydrolysis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>HCl</td>
</tr>
<tr>
<td>p.t.f.e.</td>
<td>Decomposed to release HF and F2 at High temp.</td>
</tr>
<tr>
<td>Nitro-cellulose</td>
<td>Oxides of nitrogen.</td>
</tr>
<tr>
<td>Nylons</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>Polyvinyl Acetate</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>Polyvinyl Acetate and Alcohol</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>Polyacetates</td>
<td>Acetic acid and Formic acid</td>
</tr>
<tr>
<td>Cold cured polyesters</td>
<td>Formic and Acetic acid</td>
</tr>
<tr>
<td>Phenolformaldehyde</td>
<td>Ammonia and Formaldehyde</td>
</tr>
<tr>
<td>Epoxides</td>
<td>Amines may be evolved from cold cured epoxides &amp; HCl from epichlorhydrin</td>
</tr>
<tr>
<td>Rubber</td>
<td>Formic and acetic acid evolved from non-vulcanised &amp; H2S,S02 from vulcanised rubber</td>
</tr>
</tbody>
</table>
### Table 1.2

<table>
<thead>
<tr>
<th>Mechanisms</th>
<th>Failure</th>
<th>Rate factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption Volume Wicking</td>
<td>Low insulation Resistance (IR)</td>
<td>High Temp.</td>
</tr>
<tr>
<td></td>
<td>Low Dielectric strength (DS)</td>
<td>High rh</td>
</tr>
<tr>
<td></td>
<td>High Loss Factor (LF)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Changes R, L, C, O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Leaching of lower polymers</td>
<td></td>
</tr>
<tr>
<td>Absorption (Surface)</td>
<td>Arcing Tracking</td>
<td>Temperature</td>
</tr>
<tr>
<td></td>
<td>changed IR, DS, LF</td>
<td>Cycling, Contaminants, Corrosion, Fungus, Salt, Dust</td>
</tr>
<tr>
<td>Wetting &amp; Drying Cycle</td>
<td>Excess of moisture trapped in poorly sealed enclosures, aging effect, crazing, cracking, mechanical loss.</td>
<td>Temperature cycling, ON/OFF eqpt., duty cycle.</td>
</tr>
</tbody>
</table>
REFERENCES


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FILM BREAKDOWN

Aqueous solution of sodium chloride and air

\[
\begin{align*}
\text{FeCl}_2 + 2\text{NaOH} & \rightarrow \text{Fe(OH)}_2 + 2\text{NaCl} \\
\text{Fe}^{2+} + 2\text{Cl}^- & \rightarrow \text{FeCl}_2 \\
\text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + 2\text{e}^{-} \\
\text{Cl}^- \quad \text{ions} & \quad \text{Na}^+ \quad \text{ions} \\
\text{Fe}^{2+} \quad \text{ions} & \quad \text{Na}^+ + \text{OH}^- \rightarrow \text{NaOH} \quad \text{OH}^- \rightarrow \text{H}_2\text{O} \\
\text{Fe}^{2+} + 2\text{OH}^- & \rightarrow \text{Fe(OH)}_2 \\
\text{H}^+ + \text{e}^- & \rightarrow \text{H} \\
\text{O}_2 & \rightarrow 4\text{H}^+ + 4\text{OH}^- \\
\end{align*}
\]

* \(4\text{H}_2\text{O} \rightarrow 4\text{OH}^- + 4\text{H}^+\) discharged
thus: \(4\text{H}^+ + 4\text{e}^- \rightarrow 4\text{H}\)
This leaves corresponding excess of \(\text{OH}^-\) ions. The cathode is depolarised through adsorption of \(\text{O}_2\), the effect being \(4\text{H} + \text{O}_2 \rightarrow 2\text{H}_2\text{O}\) and \(2\text{H}_2\text{O} + 4\text{e}^- + \text{O}_2 \rightarrow 4\text{OH}^-\)

FIG. 1.1
(a) STRESS CORROSION OF LEAD WIRE

(b) 2N2273 TRANSISTOR (MOUNTED)

STRESS CORROSION CRACKING OF A KOVAR LEAD WIRE IN A PRINTED CIRCUIT BOARD

(REPORT: U.S. ARMY ELECTRONICS COMMAND, 1973)

FIG. 1.2
The predicted deterioration by corrosion after five years exposure in India. The predicted deterioration is defined by duration of exposure in constant chamber conditions with temperature 40°C and relative humidity 98%. The prediction is related to clean atmosphere and data are applicable for steel.

Predicted corrosion of steel

Fig. 1.3
THE PREDICTION OF DETERIORATION BY MICROBIAL ACTION AFTER ONE YEAR EXPOSURE IN INDIA. THE PREDICTED DETERIORATION IS DEFINED BY DURATION OF EXPOSURE IN CONSTANT CHAMBER CONDITIONS WITH TEMPERATURE 30°C, RELATIVE HUMIDITY 100% AND USUAL MICROBIAL INFECTION GIVEN BY I.S.O. AND IT IS EXPRESSED IN HOURS. THE DATA ARE APPLICABLE FOR MATERIALS LOW RESISTANT AGAINST MICROBIAL ACTION, THAT MEANS THE MATERIALS IN WHICH PREVAILING COMPONENTS ARE NATURAL ORGANIC BASES.

PREDICTION OF DETERIORATION BY MICROBIAL AGENCIES

FIG. 1.4
PREDICTION OF DETERIORATION LAMINATED AND MOULDED MATERIALS

THE PREDICTION OF DETERIORATION BY WATER VAPOUR SORPTION AFTER FIVE YEARS EXPOSURE IN INDIA. THE PREDICTION DEFINED BY DURATION OF EXPOSURE IN CONSTANT CHAMBER CONDITIONS WITH TEMP. 40°C & RELATIVE HUMIDITY 98% & IT IS EXPRESSED IN MONTHS. THE DATA ARE APPLICABLE FOR MATERIALS WITH SORPTION ISOTHERM CURVE OF THE SAME SHAPE AS THAT OF THE CURVE A & WITH THE CURVE OF DEPENDENCE OF DIFFUSION COEFFICIENT ON TEMP. OF THE SAME SHAPE AS THAT OF CURVE B (FOR EXAMPLE FOR LAMINATED & MOULDED MATERIALS).