

DETERIORATION OF MATERIALS IN STORAGE

AND

RECOMMENDED STORAGE CONDITIONS

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PROGRESS REPORT VI
DETERIORATION OF MATERIALS IN STORAGE
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INTRODUCTION

This progress report is a summary of much of the information published in Progress Reports II and V both of which concern the survey of technical literature on the general subjects of dehumidification and deterioration of materials. The entire search of published literature, both in catalogued library material and Government Research Reports, has dwelt mainly on the acquisition of information on dehumidification, dehumidified storage, the effect of different methods of storage on the preservation of material and equipment, different methods of storage used by industry and government, and optimum storage conditions for different types of materials.

In addition to the literature summarized in Progress Report II and V, this report contains additional information which has been reviewed since writing these reports in order that certain portions of the contract scope of outline can be satisfied. Therefore, this report deals mainly with the fundamental factors causing deterioration, the effect of climatic conditions on materials in storage, and the recommended storage conditions for different types of materials.

It can be well understood that the discussions of the basic principles of corrosion and deterioration cannot be treated in entirety in a report such as this because of the magnitude of details that the subject embraces. The factors and details of main concern here are those which are encountered with materials in storage and the highlights of the factors causing deterioration are presented along with the methods by which deterioration of material

in storage can be controlled. There are many environmental factors which must be considered differently depending upon how materials are exposed. Therefore, many of the predominant factors promoting corrosion and deterioration are either suppressed or excluded in many types of storage containers or storage environments.

In order that this report can be complete in its objective, the first portion of the report is devoted to discussions on the fundamental concepts of corrosion and deterioration of materials. In this discussion, materials have been grouped according to two general classifications - metal and organic materials. It is not altogether correct to say that materials in these classifications deteriorate by two separate or distinct causes, however, it can be generally stated that metals deteriorate primarily by a process known as the electrochemical processes while organic materials generally undergo deterioration due to chemical reactions. For this reason it is considered that the significant mechanisms of each can be discussed without serious overlap.

As previously mentioned, many of the factors which are influential in some process of deterioration are everywhere present in the atmosphere and therefore are present with materials in storage. In order that these factors can be evaluated under such conditions they are discussed individually to bring out circumstances under which they must be considered in the prevention of deterioration. Climatic factors are not always present in the same degree nor do they act with the same degree of activity. However, the degree in which they are in combination can be responsible for accelerated deterioration or be the cause of some other indirect degradation of material.

The last portion of the report gives the type of environment most suit-

able for the storage of different types of materials. The materials are discussed as general classes since it is not always possible to make distinctions within a group. For example, plastics, of which there are numerous types differing widely in physical and chemical properties, cannot be treated collectively since each type requires individual consideration. For a material such as plastic only the general factors which affect all types are discussed and the recommended conditions for storage are those which would be most suitable to all of the different plastics. In many cases it has been possible to draw from published literature specific storage conditions for materials. In cases where no specific storage conditions are given in the literature, those presented here are felt to be most suitable based upon information concerning the factors which cause and promote deterioration.

True optimum storage conditions for all types of materials will become better known because it has only been during recent years that extensive studies have been devoted to this subject. Those materials for which no information is published will undoubtedly be the subject of future studies of this nature. Since true time exposure studies are time consuming, storage exposure tests should be initiated promptly in order that the field of preservation-in-storage can advance to meet the requirements of all different types of materials now in use. As new construction materials appear in use, they should likewise be subjected to long term storage exposures in order that storage requirements will be developed to serve future needs. Those responsible for the storage of materials are handicapped because when manufactured goods reach them, they are not in the position to make major alterations on the item to make it more suitable

for long term storage. They are confronted with the problem of maintaining the item in storage to the best of their ability within practical and economic means.

DETERIORATION OF METALS

METAL CORROSION

When metals are placed in contact with water or a solution, there is a tendency for electrically charged metal particles (ions) to go into solution. Because the solution must remain electrically neutral an equivalent number of positive ions of another element must be displaced. In the case of a metal such as iron in water, hydrogen is plated out on the surface of the metal as a thin invisible film.

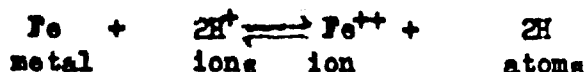
The thin film of hydrogen may retard the reaction by insulating the surface of the metal from the solution. Further buildup of the hydrogen film will cause positive hydrogen ions to re-enter the electrolyte solution which results in reducing the entrance of the electrically charged metal ion to the solution. Further reaction depends upon the success in removal of this hydrogen film. The removal is generally afforded by either its combining with oxygen in the solution to form water or by escaping from the solution as bubbles of hydrogen gas. Regardless of the process of hydrogen removal the reaction is permitted to take place as more metal ions may go into solution and more hydrogen may be plated out. Generally, the removal of the hydrogen film is determined by the concentration of dissolved oxygen in the solution which in turn depends upon the degree of aeration, flow, temperature, etc., of the water.

The tendency of hydrogen to plate out as gaseous bubbles from a solution increases with the degree of acidity of the solution. Thus corrosion is generally more rapid in acid solution and less rapid in alkaline solution.

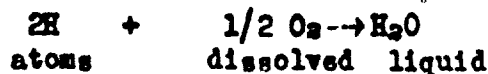
The initial regions of corrosive attack upon a metal are dependent upon the stability and continuity of the initial oxide film which is formed on metals upon exposure to the atmosphere. There are, however, many other

factors which determine and control the process of corrosion which will be discussed in detail later.

The process of electrochemical corrosion can be most easily understood with reference to the simplest case, that of iron. The process of electrically charged particles (ions) of iron going into solution and displacing hydrogen may be illustrated by the chemical equation:



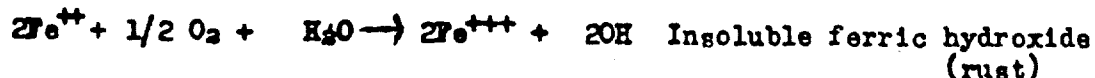
The removal of the hydrogen film is then afforded by combining with dissolved oxygen to form water:



or by escaping as bubbles of hydrogen gas:



The removal of the hydrogen film permits the reaction to proceed with the accumulation of ferrous ions (Fe^{++}) which are oxidized and precipitated as rust. The reaction being:



In this electrolytic process hydrogen acts as a metallic element with positive ions being displaced and plated out.

As previously mentioned, there are many factors which determine and control the corrosion reactions. These factors may be classified as being associated with the metal or the environment.

Factors Associated with the Metal

Electrode Potential:

The electrode potential present at any instant between the metal surface and its ions in solution is proportional to the initial tendency of

metal to corrode. Because the electrode potential may vary with the concentration of metal ions in solution, it is necessary to establish a base concentration. A standard concentration is an ion concentration of 1 mole per 1000 grams of water. With this in mind and arbitrarily establishing the potential of hydrogen as zero, the electrochemical series of elements has been arranged. Theoretically, each element in the electrochemical series should displace the elements below it; however, this may be varied by such things as changes in ion concentration, temperature and composition of the electrolyte.

Hydrogen Overvoltage:

The placing of metal in contact with water would cause a continuous evolution of hydrogen if the hydrogen were always at a potential corresponding to its position in the electrochemical series. This, however, is not always the case as hydrogen on most metal surfaces has an added resistance to overcome before it can be liberated as a gas. This added resistance is termed "overvoltage" and its magnitude depends upon the nature or condition of the conducting surface, the temperature, pressure, nature and velocity of the solution, and the size and number of hydrogen bubbles formed.

Overvoltage is then the potential which acts against the liberation of hydrogen at the cathode. Low hydrogen overvoltage in the absence of oxygen may lead to an increase in the corrosion rate. Various organic inhibitors along with other substances which are strongly adsorbed by the cathode tend to increase overvoltage with a reduction in the rate of reaction.

Nature of Metal Surface:

Non-homogeneity of metal surfaces caused by variations in compo-

sition, crystal orientation, surface finish and metal phases results in differences of potential over the metal surface. These potential differences cause the more anodic areas to be corroded instead of a uniform surface corrosion.

Intergranular corrosion is an example of corrosion over a non-homogeneous surface. Grain boundaries may be anodic to the grain body which may cause corrosion along the grain boundaries.

Ability of Metal to Form a Protective Film:

As previously mentioned, most metals are coated with an oxygen or oxide film on exposure to air which may be so impervious to passage of current that corrosion is prevented or retarded. Generally, the result is a change in effective potential to a more noble value. The property of metals to become inactive in such a manner is termed "passivity".

Metals which do not experience this sort of reaction may be protected by the addition of an inhibitor. Inhibitors are defined as chemical substances which when added to an environment decrease corrosion. A passivator is then merely an inhibitor which when added to an environment causes the metal to exhibit more noble properties.

There may be a concentration change within the electrolyte resulting from ions going into solution. This change tends to generate a counter emf which retards the reaction. This property is known as "polarization". The increase in concentration of metal ions at the anode produces anode polarization while the plating of hydrogen at the cathode may produce cathode polarization.

Factors Associated With the Environment

Hydrogen-Ion Activity:

The importance of hydrogen in the corrosion process is evident

from the primary equation. Variations in the hydrogen-ion activity then have an important effect upon the rate of corrosive reaction. The general conclusion is that the more acidic, greater hydrogen-ion activity, the greater is the corrosive attack. This, however, is not always true as many metals have a tendency to become passive upon oxidation in concentrated acids. Aluminum and many alloys are unaffected by variations in acidity as a result of their inherent passivity. Although most metals are more strongly attacked by acids, the amphoteric metals (aluminum, lead, zinc, etc.) are corroded in alkalies.

Influence of Oxygen in Solution:

Because the rate of corrosion is dependent upon the success in the removal of the hydrogen film from the cathode, the importance of oxygen in the solution can be understood. Oxygen in solution will remove the hydrogen by combining with it to form water. The rate of corrosion is therefore controlled by the amount of dissolved oxygen adjacent to the metal surface.

Although an increase in oxygen concentration usually increases corrosion some metals require an excess of oxygen to remain more passive. This is true of such metals as aluminum and many of the stainless steels which may corrode when the oxygen concentration is small. Corrosion of metals may take place in low oxygen concentrations when conditions exist that will cause removal of hydrogen or attack by other ions.

Effect of Other Ions in Solution:

The presence of ions other than the metal or hydrogen ions can affect the rate and degree of corrosion. Probably the most important

influence of other ions is the resulting nature and distribution of corrosion products. An example of this would be the protective coating formed on deposition of calcium carbonate from hard water. Secondary effects could be the modification of metal and hydrogen-ion concentration by the presence of other ions or direct metal oxidation by the other ion itself.

Temperature:

The most important effects of temperature on the corrosion of metals are its relation to solubility and chemical reactions.

An increase in temperature generally increases the rate of chemical reactions and reduces the solubility of gases in solution. Changes in temperature may also affect the solubility of reaction products in such a manner as to change the nature of the corrosion products.

Summary:

The corrosion of metals is most explainable by the electrochemical theory with the initial attack being dependent upon the nature of the original oxide film already on the surface of the metal. Further attack is controlled by the previously mentioned factors associated with the metal surface or the environment.

Factors associated with the environment are encountered in storage of metals as climatic factors of moisture, temperature, oxygen and atmospheric contaminants. Those factors associated with the metal are concerned mainly with the type of metal and its surface condition.

PREVENTION OF METAL CORROSION

In order to prevent corrosion of metals, control must be exerted over the influencing factors. The prevention of metal corrosion during indoor

storage relies upon the use of various coatings, inhibitors and passivators, and dehumidification.

Inhibitors, passivators, and coatings may reduce the corrodability of the metal, the corrosiveness of the environment, or act merely as a mechanical barrier against the corrosive medium. Dehumidification relies upon the fact that moisture is required in the corrosion process and its removal will inhibit or greatly retard the process.

Metallic Coatings:

There are basically two types of protective metallic coatings used on corrodable metals, one type being cathodic and the other anodic to the base metal.

Cathodic coatings supply the metal surface with a more noble metal resulting in reduced corrosion. Pinholes and discontinuities within a cathodic coating tend to cause an acceleration of localized corrosion. Corrosion is accelerated at points where the base metal is exposed, as a small anodic area is present in the electrolyte with the cathodic coating providing a suitable surface for the deposition of hydrogen. Care must therefore be used in the application of cathodic coatings and in some cases it may be advisable to apply an outer insulating coating.

Anodic coatings, being more anodic than the base metal, are preferentially attacked in the electrolytic process. It is in this manner the anodic coatings exhibit their protective properties with eventual destruction of the coating. Unlike cathodic coatings, they will protect exposed surfaces of the base metal from some distance away depending upon the conductivity of the electrolyte and the metals concerned. This type of coating should be chosen where the protective coating is likely to be broken or contain pinholes.

There are many different methods of applying metallic coatings such as metal spraying, dipping, electrodeposition, deposition from a vapor and metallurgical bonding by rolling, to name a few. Probably the most common methods are electrodeposition, and sprayed and hot dip coatings.

The selection of the coating should include consideration of its durability, adhesion to the base metal, cost and ease of application, its uniform density and continuity, and the final appearance desired. In the practical application a compromise must be made after consideration of the cost and type of exposure, as none of the coatings exhibit all of these desirable properties.

Organic Coatings:

Organic coatings are widely used in the protection of metal surfaces from atmospheric corrosion. They act as mechanical barriers preventing the corrosive mediums from reaching the metal surface. The performance of an organic coating is therefore largely dependent upon its permeability and ability to adhere to the metallic surface and in many cases it is necessary to apply more than one coat to obtain satisfactory results.

The application of paint coatings is usually preceded by an application of an undercoat or primer coating. Although the primer coat provides a base for the barrier coat, permitting maximum adhesion, it often supplies an inhibiting or passivating effect against any corrosive media, which may permeate the barrier coat.

Other than the coating selection the most important means of assuring satisfactory results is proper application and surface preparation. Prior to the application of the primer and protective coating, metal surfaces should be free of mill scale, oil, grease, corrosion products and dirt.

Cleaning of the metal surface may be accomplished through the use of acid and alkaline treatments, organic washes, and mechanical abrasion.

In many cases a passivating treatment may be given the metal after cleaning. This is especially advantageous on very active metals such as magnesium, aluminum, zinc and steel. An example of the passivation treatments would be the use of a phosphate coating on steel which converts the steel surface to the less active metallic phosphate.

After cleaning, passivating, and priming of the metal surface the organic protective coating may be applied. The most commonly used coatings are lacquers, varnishes, enamels, and various special finishes such as baked resin finishes which are used without a primer coat.

Inhibitors and Passivators:

An inhibitor may be defined as any chemical substance or mixture that effectively decreases the corrosion rate when added in small amounts to a corrosive environment. Inhibitors tend to decrease the rate of current flow in the system by increasing anodic or cathodic polarization. Those inhibitors which increase anodic polarization are known as anodic inhibitors while those acting upon the cathode are appropriately termed cathodic inhibitors.

The type of material to be protected and the environment to which it is subjected must be thoroughly understood before the selection of the inhibitor can be made. An inhibitor may effectively decrease the corrosion of a metal in one environment and actually promote corrosion of the same metal in a different environment. In some cases, an inhibitor may decrease corrosion and at the same time promote localized pitting.

Passivators are inhibitors which change the electrode potential to a

more noble value. The tendency of an anodic inhibitor to act as a passivator is greater than that of a cathodic inhibitor. The ability of an inhibitor to act as a passivator as well as the amount of inhibitor required are dependent upon the type of metal, the environment, and the temperature.

Various long-chain nitrites referred to as volatile corrosion inhibitors have experienced limited use in the protection of metals, mainly ferrous metals. The compounds are used as either a powder or impregnated on a carrier such as fiberboard or paper. When enclosed in a space with the material to be protected, the molecules migrate to the metal surface in a vapor phase thus resisting the access of water to the surface. The use of VCI requires tightly sealed containers, relatively impermeable to water and corrosion inhibitor transmission.

Dehumidification:

Dehumidification is a method of preventing metal corrosion by reducing the amount of water vapor which is in the air. By proper humidity control it is possible to keep the moisture content of air at a level low enough so that corrosion is not promoted. The term humidity control applies equally to both air conditioning processes of humidification and dehumidification. These two processes are differentiated by the fact that one adds moisture and one removes moisture from the air and dehumidification is a process in which moisture is continually removed from air to maintain a desired relative humidity.

DETERIORATION OF ORGANIC MATERIALS

FACTORS IN THE DETERIORATION OF ORGANIC MATERIALS

The materials of organic nature undergo degradation or deterioration by a means unlike that described for metals. The general theory covering the deterioration and corrosion of metals falls under the category of electrochemical process.

The basic unit of composition of many organic materials is either cellulose or hydrocarbon derivatives and they can be affected by numerous chemical and physical factors. Upon exposure to undesirable combinations of these factors a chemical change takes place which results in some change in physical properties of the materials. The changes brought about by the factors are not common to all materials and likewise the degree of exposure to such factors produces varied results. The chemistry involved in the chemical changes taking place in the deterioration of organic materials is extremely complicated and cannot be discussed in detail in this report; however, it is intended that this discussion will cover the highlights of most organic materials and the factors which are primary in causing deterioration.

The organic materials which are of primary interest in this report are such materials as wood, paper, textiles, plastics, rubber, and leather.

Wood

The deterioration of wood in general is defined mainly by the end use of wood and the type of exposure to undesirable elements. The two main phases of wood deterioration are; (1) Deterioration in physical form - warping, cracking, crazing, and (2) deterioration due to fungi, micro-organisms and insects. Cracking and crazing of wood results from

improper seasoning and storage, while deterioration by fungi and insects is inherent in wood and wood products.

There are two main types of wood harming fungi; (1) the wood destroying fungi and, (2) the wood staining fungi. The wood destroying fungi are capable of disintegrating the individual wood cells which results in both physical and chemical changes in the wood. These changes are often referred to as decay. The wood staining fungi cause only discoloration in wood without causing a change in physical properties. Both the wood destroying and wood staining fungi are low forms of plant life which infect all types of wood. Fungi are unlike green plants in that they cannot make their own food, but must have a supply available. In wood this food supply is stored in the wood cell walls. The growth or development of fungi requires favorable temperature and moisture conditions, plus food supply and air. The food for growth comes from the wood itself while the other growth requirements are factors of the environment. In the absence of any one of the growth requirements the fungi development may be retarded or even stopped for extended periods, however, when favorable growing conditions are provided the dormant fungi will be revived. Generally, the most suitable moisture conditions for fungi growth in wood is a moisture content above the fiber saturation point (25% - 30%). The most favorable temperature for fungi growth is in the range of 75°F - 90°F.

Wood at one time or another is exposed to infection by some type of fungi and because of this, deterioration can always take place when conditions are favorable. There is little that can be done in the way of sterilization to kill fungi because subsequent exposure will contaminate the wood.

Insects are another primary cause of wood deterioration and like fungi are difficult to control. Again, the degree of exposure and the use of the wood defines largely the susceptibility of attack by insects. The most predominant insect causing deterioration of wood is the termite. It requires favorable temperatures and moisture conditions to sustain its life.

Wood is relatively unaffected by normal variations in temperature. Temperature in combination with humidity determines the moisture content of wood but in this case temperature is of secondary importance. Light, like temperature, has little effect on wood other than being indirectly necessary for fungi growth.

Paper

Paper, like wood, has cellulose as its basic unit of composition. Because of this it is susceptible to the same types of deterioration as wood plus deterioration by other factors. In addition to deterioration caused by biological agents, paper is deteriorated by physical agents, chemical agents, and manufacturing constituents. The biological agents consist of insects, micro-organisms, and rodents. The physical agents are sunlight, heat, dust, and dirt, and moisture. Chemical agents consist of atmospheric smoke and gases. Manufacturing constituents are deleterious chemicals used in processing paper.

Paper, because of its uses, is not subjected to the large degree of infestation by cellulose feeding micro-organisms such as wood is. Consequently, deterioration due to fungi is not considered a primary deterrent because fungicidal treatments of paper are simple and effective. Paper is more susceptible to deterioration when exposed to physical agents. Changes in paper which take place upon exposure are photochemical, oxida-

tive, hydrolytic, and other chemical changes. These changes are oftentimes referred to as "Natural Ageing". These changes result from exposure to light, heat, moisture, and acidic atmospheric gases. The rate of any chemical change depends largely upon the degree of exposure. Of the factors listed above exposure to sunlight is probably the most harmful. Cellulose in paper is deteriorated by the ultraviolet portion of the spectrum and it is evidenced by discoloration, embrittlement, and loss of tensile strength. Heat and water vapor tend to increase the action of light on paper deterioration.

Paper exposed to heat (moderate) alone does not suffer appreciably. The next most harmful exposure is in an atmosphere contaminated with sulphur dioxide. Paper exhibits an increase in acidity and a decrease in folding endurance when exposed to sulphur dioxide. The presence of deleterious material in the paper from manufacturing is directly related to the quality of paper. The cheaper papers having more contaminants and consequently undergoing more deterioration.

Ordinary paper may be differentiated from wet-strength paper on the basis of the effect of excessive moisture. Many types of untreated papers lose their structural strength and the fibers fall apart due to the solvency of the gelatinous bonding material in water. Wet-strength papers have the advantage of being able to withstand excessive moisture.

TEXTILES AND CORDAGE

For the most part textiles are composed of organic materials and they undergo degradation in the same manner as other organic materials. The natural fibers used in textiles consist of cotton, wool, linen, and silk. The synthetic fibers consist of viscose, acetate, rayon, polyvinyl, and

polyester. Another synthetic fiber, not organic in character, is glass fibers which are now used in textile manufacture. Cordage is made largely from natural fibers of jute, Manila hemp, American hemp, sisal, and ramie.

Textiles are caused to deteriorate by either biological agents or chemical-physical agents. The biological agents are principally micro-organisms (fungi and bacteria) and insects. The chemical-physical agents are sunlight, oxygen, moisture, temperature changes, and other components of the weather.

It is not possible to evaluate the deterioration of textiles in terms of any one agent or by segregating the agents of deterioration into a class of primary or secondary causes. The action of biological agents and exposure to the chemical-physical agents constantly causes reactions and it is only the rate of the reaction that can be changed by environment control. Organic reactions require two reactants and in the case of textiles the fibers themselves are one reactant and any of the deteriorative agents previously mentioned constitutes the other reactant. By altering the conditions required for a reaction to occur, the rate of reaction can be reduced and if carried out to the limit the reaction may be stopped entirely.

Textiles, like paper, are affected by light exposure and in particular the ultraviolet portion of the spectrum. Most textiles exhibit a loss in tensile strength on exposure to light. Dyes are also affected by light exposure with a resulting change in color. Acidic contaminants in the atmosphere have a rapid effect on various textiles and it has been found that the tensile strength of cotton varies with acidity of the atmosphere.

Plastics and Rubber:

The deterioration of plastic and rubber materials is difficult to describe without becoming involved in lengthy discussions of each individual compounding. Plastics and rubber are usually considered in the same light because they have basically the same molecular construction. They are referred to as polymers of high molecular weight. Today most plastic materials, including some types of rubber, are synthesized and have properties much the same as materials made from natural sources. The field of polymer chemistry has in the past few years developed into a large industry and it is now possible to synthesize materials having properties to meet end use requirements including resistance to many phases of deterioration.

In the compounding of the various plastics and rubber, additives such as fillers, plasticizers, pigments, vulcanizers, stabilizers, and dyes are used. These materials must be considered along with the basic composition since they are, in many cases, involved in the overall deterioration process. It follows that each individual compounding must be considered for different exposures and the deterioration that results.

Chemical and physical deterioration of organic plastics results in cracking, reduced strength, warping, and loss of transparency. The physical changes usually result from loss of plasticizer and exposure to cyclic humidity conditions. Chemical changes in polymers depend to a large extent upon the basic design of the polymer. Polymers are classified in two main groups according to the molecular structure - (1) linear or chain polymers and, (2) branched network polymers. The linear polymers are often referred to as thermoplastics and the branched polymers as

thermosetting polymers. The strength of linear polymers is dependent upon the size of molecule and interchain forms within the individual molecules. The number of cross-links in linear polymers is small compared with the branched network thermosetting polymers.

The linear thermoplastic polymers may deteriorate in any of three ways: (1) the chains may be divided into smaller segments, (2) the chains may be tied together by cross-links or, (3) the nature of side groups may be changed.

Since linear polymers are essentially long-chain molecular polymers, cutting the length of the chain is the most important since this reduces the size of the molecule which in turn results in decreased strength. The second condition which results by introduction of cross-linkages is not as important since higher strength may be induced but if carried to extremes will cause a loss of elasticity, shrinkage, and cracks. The third factor which is a change in the structure of side groups can result in a degradation of certain properties such as electrical properties, moisture absorption, and others, although no serious effect is noticed with the strength properties. Thermosetting plastics are not greatly affected by the first two types but the modification of side groups may cause surface deterioration on exposure to weather.

As discussed for other organic type materials, the organic compounds including those of plastic and rubber are susceptible to reaction with various factors of the environment such as water vapor, ozone, and oxygen. These agents, among others, cause a deterioration of plastics upon exposure to the weather. Of the three, the most important in the process of deterioration is oxygen and second in importance is ozone. These two

elements will cause a change in molecular structure which in turn results in changes in physical properties. The degree of exposure determines to a large extent the rate of deterioration. Also, the chemistry of the material determines to a large extent its susceptibility to deterioration by oxygen or ozone. Oxygen and ozone promote reactions which are irreversible and once the reaction has started little can be done to activate any change in the opposite direction.

The effect of water vapor on rubber has been found to be of secondary importance and at present there are diverse opinions as to which agent - Oxygen or Ozone - is the primary cause of rubber deterioration. The rate and degree of deterioration of rubber varies according to type and composition. Exposure of rubber to light is known to cause cracking and crazing but the primary deteriorant - oxygen or ozone is not definitely established. There are opinions that the most severe agents in deterioration of rubber are ozone, heat, and oxygen in that order and recent use of antioxidants has shown that ozone and heat are more important in the degradation process than oxygen.

The exposure of plastics to ultraviolet results in cracking and crazing. Light in combination with other physical and chemical agents will cause discoloration, embrittlement and a general loss of properties in plastics. The degree of deterioration depends largely on the type of plastic.

Paint Films:

The most degenerative source of moisture on paint films other than immersion in water is moisture condensation. This is because condensation does a thorough job of wetting the surface. Along with condensation,

deterioration of paint film is also evident in the adsorption of water. Many paint vehicles are solvent in water particularly cellulose derivatives and other vehicles to a varying degree. Much paint failure due to water has been eliminated through the development of highly insoluble pigments and very impermeable vehicles.

Low temperatures cause most paints to become brittle, however, paint films at lower average temperatures show better ageing characteristics. Variation in the thermal expansion of paint and the painted surface may cause cracking and checking of the paint under varying temperature conditions. Increased temperatures cause an increase in chemical destruction of the paint films.

Like textiles, dyes, plastics, and rubber, paints and lacquers are seriously affected by photochemical activity of sunlight. Paints compounded of various zinc oxides and titanium dioxide exhibit chalking on exposure to light. Besides the photochemical deterioration of pigments, radiant energy from sunlight acts as a catalyst in the chemical degradation of the various paint components.

Oxidation of paint films is greatly increased with the presence of heat, moisture, and light. Although oxygen is required in the drying of paints further oxidation results in brittleness, cracking, scaling, and chalking.

Paints containing pigments of white lead are very reactive to sulfur dioxide and hydrogen sulfide. In the presence of moisture the sulfur compounds react with white lead to form a dirty black lead sulfide. There are, however, many paints such as those using titanium or zinc pigments which will withstand such deterioration.

Leather:

Finished leather is an end product of animal skins which has undergone chemical and mechanical changes to improve its stability. The chemical and mechanical treatment of leather is known as "tanning". It is through tanning that leather derives its ability to withstand deterioration from different elements. The major deterioration of leather is due to a chemical process called hydrolysis. The chemical change occurring during the process of hydrolysis involves water and therefore moisture content of leather is an important factor in this type of deterioration.

It is possible to more or less custom-make or tan leather to give resistance to various elements by altering the tanning process.

Glass:

The composition of glass is primarily inorganic material and it cannot be classified either as a metal or as an organic material. Glass, as a material of construction, is subject to deterioration and the factors causing its deterioration are the same as those of other materials. Normally, glass is thought of as being a very stable material and relatively unaffected by moisture, heat or light. Certain constituents of glass are, however, affected by moisture and the deterioration of glass is primarily a surface deterioration in the form of fogging. The surface of glass does absorb moisture and also a glass surface is easily wetted. When water comes in contact with the surface of glass, certain constituents which are water soluble migrate to the glass surface and crystals of hydroxides and carbonates form. The rate at which these deposits are formed is a function of relative humidity with the higher rate of formation being at the higher relative humidities. Tests have shown that the

rate of deterioration is extremely low with the humidities at 60 per cent or below.

The majority of deterioration of glass surfaces has been noted on highly ground glass lens elements in optical instruments. Fungi and biological agents have also been found to deteriorate glass surfaces of this nature.

Summary:

The previous discussions for individual materials of organic origin represent a summary of information available on the factors causing deterioration of these materials. Most of the literature also presents the factors associated with and responsible for the deterioration of equipment such as electrical equipment and optical and photographic equipment. Electrical equipment in general consists of a combination of organic materials and metals assembled together. It follows that the basic materials of construction are affected by the same physical and chemical agents but the operation of the assembled unit is also affected by these agents. This type equipment when exposed to excessive moisture not only undergoes metal corrosion, insulation deterioration but electrical properties and performance are affected.

Optical and photographic equipment is caused to deteriorate primarily by exposure to heat and moisture. Photographic film and paper is seriously attacked by high temperature and high relative humidity. It causes a reduction in film quality, and film speed. Optical glass, while not being of organic origin, is seriously deteriorated by moisture. The reason for this degradation is that most glasses have constituents which are soluble in water. The soluble substances migrate to the glass surface in the presence of

excessive moisture and result in fogging the glass. The amount of fogging depends on the type of glass and the amount of water present. Fine optical glass is attacked by atmospheric contaminants and its effect is a change in refractive index.

PREVENTION OF DETERIORATION OF ORGANIC MATERIALS

The deterioration of materials of organic origin is to a large extent dictated by the end use of the material and the degree of exposure to which the material is subjected. By anticipation of the end use of the material it is possible to add or provide resistance to exposure and thereby increase the useful life of the material. Many organic materials cannot be treated in a manner similarly used for metals by protective coatings and surface treatments. It is possible during the manufacture and processing of organic materials to provide additives and other treatments to improve resistance to various undesirable elements of exposure.

Since most of the organic materials are susceptible to deterioration by fungi and micro-organisms it is possible and in many cases carried out with a treatment of fungicides to give resistance to this cause of deterioration. Materials such as textiles, wood, leather, and paper and some plastics are generally treated with a fungicide if it is anticipated that such materials will be used where attack by fungi is possible.

To give added resistance to materials which are affected by exposure to the physical elements such as heat, sunlight and moisture, additives are added which tend to retard the chemical reaction which takes place when these materials are exposed. These additives cannot be described individually because of the nature in which they are applied, however, their use or application can generally be made only

at the time of manufacture.

The more positive control of deterioration with organic type materials is to eliminate or reduce to a minimum the degree of exposure to the most undesirable elements. In storage of such materials it is possible to reduce the degree of exposure to some elements, but environmental control is applied only to the extent that it is economically feasible to do so. Inasmuch as all materials are in one way or another affected by moisture it is most practical to maintain control of this factor and thereby reduce deterioration as much as possible. The most detrimental factors are moisture, oxygen and sunlight. Since it is not possible to exclude oxygen from the atmosphere by any practical means, the main consideration is the control of moisture. By controlling the moisture conditions within an environment and excluding sunlight two of the factors which promote a chemical reaction have been subdued and the result is a decrease in the rate of any chemical reaction which occurs. Also, a control of moisture can limit and in many cases inhibit the growth of fungi which depend upon moist environments for existence.

Much can be done in the storage of materials of organic nature if dust, dirt and other debris are not allowed to be in contact with the materials. These are objectionable from the standpoint of being contaminated, in addition to being attractive to insects and rodents.

EFFECT OF CLIMATIC CONDITIONS

The intensity of the deteriorative attack by the physical, chemical and biological agents of deterioration is, for the most part, dependent upon the prevailing climatic conditions for any given locality. The climatic variables most concerned with material deterioration are moisture, temperature, light, atmospheric oxygen and ozone, air contaminants, dust, dirt, and sand.

Each factor makes its own contribution to material deterioration, however, they never occur singly in the atmosphere. Many times it is the combination of variables which determine the seriousness of attack. In order to facilitate the discussion, each variable will be discussed separately.

Much of the information available on the degradation of materials by exposure to climatic variables is in reference to extreme climatic conditions. The interpolation of this to the moderate climatic conditions as experienced in warehouse storage is quite difficult. The scope of this report has also eliminated discussion of the highly complex chemical changes which take place in many materials subjected to the various chemical and physical agents of deterioration. The extent of deterioration by climatic factors not only depends upon the degree to which they appear separately but more important upon the degree to which they appear in combination. Many materials are little affected by a single climatic variable but may be seriously affected when this variable is combined with another deteriorative agent.

Moisture

Moisture alone is not considered a deteriorative factor, although, when

in combination with other agents it exhibits highly degradative properties. Moisture in either liquid or vapor form is a necessary agent for almost all forms of deterioration.

Water is one of the best chemical solvents known, being able to dissolve many chemicals and bring them into contact with the surface of the material causing damage. It may combine with an industrial air contaminant such as sulfur dioxide and form sulfurous or sulfuric acid which is very destructive to most materials. Although water is fairly stable it is capable of promoting reactions between substances and entering into various other chemical reactions.

The electrochemical process, the principle cause of corrosion of metals, relies upon the presence of an electrolyte which in most cases is afforded by water or water in combination with various chemicals. The absence of water from an electrolytic reaction will retard or stop the process.

Water is also a necessity in all life processes. This being true, it is seen that biological growth which is a cause of deterioration in many materials is dependent upon a supply of water. Biological growth in and around material may be controlled to a varying degree by controlling the amount of water present. It has been found that very little fungal growth is ever present at relative humidities below 70%.

Water may be present on a material as either free water deposited by condensation or as adsorbed water due to the hygroscopic properties of the material. The degradation due to moisture adsorption may be of a physical nature resulting in shrinking or swelling as water is given off or taken on by changing temperatures and humidities. Alternate shrinking and swelling may cause warping of various materials. In many cases, stresses are set up

within the material which may cause fracture of the material or of adhesives at joints.

Temperature

Temperature affects material degradation in several ways. Besides combining with the other climatic variables in causing deterioration, temperature extremes and variations may cause dimensional changes in the material, loss of the useful properties exhibited at ordinary temperatures, and a control in the rate of chemical reactions.

As most materials are non-uniform heat conductors, temperature changes set up a temperature gradient through the material which results in varied internal stresses. These internal stresses caused by dimensional changes may cause rupture of the material depending upon its particular properties. This is particularly true when there is a combination of materials having different coefficients of thermal expansion and a temperature gradient causes a dimensional change in one material which applies stress upon the others.

In the case of deterioration by a chemical process it can be generalized that the reaction rate doubles for every 10° Centigrade rise in temperature. Therefore, most deterioration is increased upon heating and decreased on cooling. The reasons for this is probably that most materials and chemicals have increased solubility and are more susceptible to reaction with water and oxygen at elevated temperatures. Many organic materials may also undergo internal chemical changes at elevated temperatures.

Although temperature somewhat affects the degree of biological attack the range at which it retards growth is at the outer range of temperature encountered in normal storage. The optimum temperature range for most fungal

growth is from 50° - 90°F.

Dimensional changes are generally of a temporary nature unless the change has caused rupture or breakage of the material. Probably the most important effect of moderate temperatures is when it combines with the other agents of deterioration. The important physical and chemical changes in material structure are usually encountered at extreme temperature.

LIGHT

Sunlight is probably the most important factor in outdoor deterioration. Its most important effect is that portions of the spectrum alone or in combination with other agents may bring about chemical reactions in the irradiated material.

Absorption of a specific wave length by a material may cause an activation of the molecules within the material. This molecular activation may result in a loss of energy through collisions and reradiation or a chemical change in the material composition. Loss in energy results in raising the temperature of the material. The effect of temperature rise on deterioration has been previously discussed. The ultraviolet and visible portions of the spectrum (3000-8000Å) are responsible for the activation of molecules. Absorption of the infrared spectrum (8000-10⁶ Å) results in a temperature rise and no chemical reaction.

Besides causing temperature rise and photochemical reaction to take place, light has an important influence on biological growth. Many organisms are destroyed by exposure to light, particularly the ultraviolet portion of the spectrum, however, many other organisms depend upon light for their survival. Any organism which depends upon photosynthesis for manufacture of starches, sugars, and other food products cannot live without the presence of light.

The amount of deterioration produced by light depends upon the chemical structure of a material, the light wave lengths present, prevailing temperature and the degree of presence of reactive substances and agents of deterioration. In summary, light has the deterioration effect upon materials by causing; (1) temperature rise, (2) photochemical reactions and, (3) control of biological growth.

Oxygen and Ozone

All of the normal constituents of the atmosphere, except oxygen and ozone, are inert gases. At normal temperatures and pressures they will not react with substances, however, deterioration by oxygen and ozone is well known. Degradative reactions by oxygen and its allotropic form, ozone, are chemically similar. Ozone, having a much higher energy content, is a more powerful oxidizing agent with the ability to attack many materials not affected by oxygen.

As previously mentioned, deterioration by oxygen is dependent upon other physical and chemical agents. Temperature is probably the most important agent as oxidation by ozone and oxygen are chemical reactions which are controlled by temperature. The tendency is to increase the rate of reaction with the increase in temperature.

Atmospheric Contaminants

Oxygen and ozone are the only constituents of ordinary atmosphere that lead to deterioration. However, in various urban, industrial, and coastal regions there are atmospheric contaminants present which seriously affect deterioration.

The atmosphere may be contaminated with sulfates and chlorides present in the air as salt spray from sea water in coastal regions. These salts

react with water to form an electrolyte which facilitates corrosion of metals.

Urban and industrial atmospheres contain various by-products of combustion and manufacturing processes which may cause degradation of many materials. The most common contaminants are - oxides of sulfur, carbon, and hydrogen sulfide. Carbon and sulfur dioxide, when combined with water may form carbonic or sulfurous acid which are degradative to most materials. Sulfurous and sulfuric acid are more strongly ionized than carbonic acid with the result of a much stronger attack on many more materials. Hydrogen sulfide is, by itself, a strong reducing agent which reacts with most metals. Sulfur dioxide alone is a strong bleaching agent as evidenced by its use as an industrial bleach.

It may be concluded that the general effect of atmospheric contaminants on the deterioration of materials is due to their combination with moisture in the formation of acids.

Dust, Dirt and Sand

Dust, dirt, and sand may facilitate deterioration by their chemical, hygroscopic, and abrasive properties. The degree of deterioration, as is true of most agents, is somewhat dependent upon the presence of other physical or chemical agents.

Because dust and dirt are hygroscopic they will adsorb moisture from the atmosphere. In doing this, a higher moisture level is maintained on the surface of the material with a tendency to increase degradation. Fine dust is a nucleus for condensation with the ability to hold moisture in close contact with a material surface.

Dust, dirt and sands are fine organic or inorganic particles having a

definite chemical nature. Depending upon their origination they may be either alkaline or acid and provide a chemical reaction in the presence of moisture. An acid or alkaline reaction proves harmful to most materials. Highly abrasive characteristics are exhibited by dust, dirt and sand when present on moving parts or on stationary parts under other dynamic conditions such as wind. The effect of dust, dirt and sand on the various materials would then be the same as would be expected by the action of moisture or chemical reactions. The abrasive property is not important unless the material is subjected to a dynamic influence, which is usually not encountered in indoor storage of materials.

In summary, all climatic factors -- moisture, temperature, sunlight, oxygen and ozone, atmospheric contaminants, dust, dirt and sand -- promote deterioration. The degree of deterioration resulting from exposure to these elements can be determined only by defining a material in terms of its susceptibility to deterioration by any of the climatic factors. Outdoor storage of any material is the most severe exposure condition and it can be expected that all deterioration processes will proceed at a maximum rate. Any steps taken to reduce the severity of exposure will result in less deterioration. In comparing the degree of exposure in outdoor storage with that in a dehumidified warehouse, it can be readily seen that all climatic factors, except oxygen and ozone, are suppressed to the point that any deterioration process will proceed at a very slow rate. In dehumidified warehouse storage, the moisture is positively controlled, the daily temperature fluctuation is small, sunlight exposure is eliminated, and abrasive airborne sand and dirt are reduced. The remaining factors--oxygen, ozone, and dust--are of a secondary importance when the other factors, especially moisture, are controlled.

RECOMMENDED STORAGE CONDITIONS FOR DIFFERENT MATERIALS

The previous discussions in this report represent a summary of factors causing deterioration of most types of materials. In general, the rate of deterioration of any material depends to a large extent on the degree of exposure to elements which cause deterioration and also the extent to which the deteriorative factors are in combination with one another. For most materials the primary factors causing deterioration have been identified; however, the ultimate effect of exposure to these elements is not known for all cases and all types of exposure. Since these factors are always present to some degree or another, it is impractical to consider that the elimination of such variables will produce the environment necessary to give an extended or indefinite shelf life to any material. The purpose of this summary presented here is to give the information published which will provide an environment in which materials can be stored for long periods of time and a storage period in which the desirable physical properties of the materials will remain substantially the same. It is often the case that materials are said to "age" with time. The term age or ageing is adopted and used to mean some degeneration of a desirable physical property and it has been discussed in other parts of this report that the rate of such ageing can be altered by the degree of exposure to undesirable elements.

One difficulty which has been encountered in abstracting literature for desirable storage conditions for all types of materials has been the lack of data developed in tests and research studies pertaining to normal temperature and humidity conditions maintained in storage warehouses. The majority of studies which have been conducted in long term exposure of materials have been at exposures

representing extremes of climatic variables. Wherever possible the storage conditions given below have been determined from tests which approximate those to be encountered in a dehumidified storehouse. In other cases it has been necessary to interpolate or extrapolate between certain test values to arrive at a storage condition which would be considered most desirable for a particular type of material. In certain instances, specific temperature and humidity conditions are given and in other cases a range of conditions are given. The specific conditions are the most ideal but they should not be interpreted as the only condition under which materials can be stored. In defining a suitable storage environment for any material it is first necessary to know which of the physical agents is the primary cause of deterioration. Once the primary cause of deterioration is known it is then possible to assign the relative importance of control of the physical agents such as temperature and humidity. As far as materials stored in warehouses are concerned the precise control of relative humidity is of prime importance.

The conditions of temperature and humidity given are on the safe side and should give the maximum storage life in warehouse storage. It should be pointed out that storage conditions giving maximum shelf life will differ depending upon the type of storage enclosure. The temperature and humidity conditions recommended here are for storage inside large warehouses. They differ considerably from those for storage in a small package type enclosure located outdoors.

One desirable aspect of storage in large warehouses is that the daily temperature fluctuation is very small, thus making other vari-

able factors predominant. It is impossible to exclude from warehouses such factors as oxygen, ozone, atmospheric contaminants, and dust. Each of these can be considered as secondary causes of deterioration with relative humidity being the most important factor for almost all materials.

The recommended storage conditions of temperature and humidity are given below for most construction materials which are normally found in assembled units and considering such assemblies, the storage environment required for each component should be considered.

METALS. The recommended temperature for the storage of metals is approximately 75° F. and the relative humidity in the range of 40 to 50 per cent. The literature devoted to the deterioration of metals gives humidities within the range of 30 to 60 per cent, however, adequate protection is obtained in the 40 - 50% range. Although 75° F. is given as the most optimum storage temperature for metals, the normal temperatures encountered in warehouse storage are acceptable and of inconsequence providing the relative humidity is maintained constant.

PAPER. The recommended storage temperature for paper is within the range of 65 to 80° F. and the relative humidity in the range of 40 to 55%. Paper is a material which is affected primarily by exposure to sunlight and acidic gases in the atmosphere. Normally, warehouse storage does not allow exposure to sunlight; therefore one of the primary causes of deterioration is eliminated and as such, temperature and humidity become secondary factors.

TEXTILES. The recommended storage temperature for textiles is described in the literature to be cool and stable with no def-

inite temperature given. However, normal temperatures within the range of 40 to 80°F. are acceptable. The relative humidity recommended is in the range of 40 - 50% Rh. Here again textiles are predominantly affected by exposure to sunlight, atmospheric contaminants, fungi and other biological agents. Inasmuch as sunlight is eliminated in warehouse storage the control of biological agents is taken care of with a storage environment of normal warehouse temperatures and humidities within the neighborhood of 45%.

RUBBER. Recommended storage conditions for maximum shelf life for rubber is one which have a very wide diversity of opinion and no specific storage conditions are found. The literature suggests storage in a cool, dark atmosphere with temperatures in the neighborhood of 50 to 55° F. and humidities in the range of 50 to 60%. Rubber is caused to deteriorate mainly by ozone and oxygen. It is impractical to attempt any control over the ozone or oxygen content of warehouse air, and the secondary factors of temperature and humidity are not of primary concern. Indoor storage is beneficial to rubber in that sunlight, a factor promoting ozone deterioration, is eliminated and rubber is not adversely affected by the lower humidities maintained in dehumidified warehouses.

PLASTICS. No specified storage conditions for the various plastic compounds have been found in the published literature. Organic materials in general are primarily affected by oxygen. However, they are subject to microbiological attack and changes in physical properties due to extreme temperature and humidity conditions. In view of this it is recommended that plastics be stored at moderate temperatures (40-80° F) and at humidities below 70%.

LEATHER. The recommended storage temperature for leather is moderate temperatures (40-70° F) and relative humidities below 70%.

GLASS. As fogging and microbiological growth on glass surfaces are a result of high humidity, it is recommended that glass be stored at moderate temperatures (40-80°F) and at humidities below 60%.