CORROSION ISSUES IN GROUND SOURCE HEAT PUMPS USING ETHANOL BASED ANTIFREEZES

BY

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CHAPTER I

INTRODUCTION

The renewed focus on energy conservation and environmental protection in recent years has lead to an increased interest in energy efficient, environmental friendly systems. Because of this focus on conservation, interest is on the rise for innovative heating and cooling systems depending on Ground Source Heat Pumps (GSHP).

Geothermal/GSHP's provide a highly efficient space conditioning and water heating technology that can help utilities increase electricity usage, while reducing peak demand. The ground remains at a fairly constant temperature throughout the seasons, providing a higher temperature source in winter and a cooler sink in summer. GSHP's utilize this thermodynamic advantage to provide highly efficient space conditioning and water heating (1).

The GSHP circulates a heat transfer fluid through the ground loop, absorbing the earth's natural warmth in winter and rejecting heat to earth in summer. The fluid may be either a refrigerant or more commonly a secondary fluid, a water and antifreeze mixture in the heat exchanger with the refrigerant. The GSHP-systems have potential savings of 60% during the heating cycle and 25% during the cooling cycle (2).

The International Ground Source Heat Pump Association (IGSHPA), was established in 1987 in order to advance Geothermal/GSHP technology on local, state, national and international levels. The IGSHPA is based at Stillwater, OK on the Oklahoma State University campus (3).

The properties of the heat transfer fluid and the heat exchanger employed become the prime criterion for the efficient use of the system. Water may be used in heat pump systems, except in climates where the temperature during winter drops below the freezing point of water, and then antifreeze solutions are necessary. Several such antifreeze solutions have been considered and their relative merits and demerits evaluated. Glycols, a group of commonly used antifreeze solutions and methanol have been repudiated based on their relative toxicity levels (4, 5).

The cheap production of ethanol, its good heat transfer properties and environmental friendliness make ethanol a solution that can be used as an antifreeze basis in heat pumps (6). Though the use of acetates as antifreezes is recognized to be efficient and environmentally safe, their general use is restricted by high cost (4).

Besides the heat transfer properties and environmental friendliness, it is necessary for the fluid to be compatible with the materials in a heat pump system. The thrust of this research has been to evaluate and identify incompatibility and corrosion, in heat pump systems utilizing an ethanol based heat transfer fluid. Experiments have been conducted with pure ethanol to use as a comparative base for the data obtained from the experiments using denatured ethanol and a commercial ethanol based heat transfer fluid, ENVIRONOL, developed recently by Waterfurnace Inc (7). The experimental procedure used in earlier research to study the effect of acetates in general and potassium acetate, in particular, on heat pump materials has been followed in this study (8).

CHAPTER II

LITERATURE REVIEW

1. CORROSION CONSIDERATION IN HEAT PUMP

Corrosion is the destructive result of the chemical reaction between a metal or metal alloy and its environment (9). A study in 1976 showed that the economic cost of corrosion in United States alone was $70 billion annually (9). A figure of 3 - 4% of the Gross National Product (GNP) is usually accounted as the cost of corrosion annually in a developed country(10). The cost of corrosion worked on this basis would approximately amount to $200 billion in the United states for the year 1993. The indirect costs due to corrosion, involve such factors as the following (9, 10).

Plant Downtime: Besides cost of labor and parts, the loss of production during shutdown is quite enormous. A commonly cited example is the shutdown of a nuclear plant where the costs could run into millions of dollars per day (9). In the case of direct consumer related services, as in the case of GSHP's, besides replacement and maintenance costs considerable ill will be generated. In adverse climatic conditions, loss of heating or air conditioning systems could become more than irritating.

Maintenance and operating costs: Corroded parts have to be constantly replaced for the proper working of the units, and the operation of units with corroded parts is expensive and any leaks might have a considerable hazardous effect on the surrounding environment and safety of the populace. Corrosion products accumulating on heat exchanger tubing , piping and on the pumps of ground source heating systems, could decrease the efficiency of heat transfer and reduce the pumping capacity substantially.

Contamination: Soluble corrosion products in heat transfer fluid could lead to several problems in the case of heat pumps. Variations in heat transfer fluid may lead to change in chemical, physical and thermal properties, thereby reducing the working capacity of the heat pump unit.

Environmental concern: Accidents could involve spillage of the antifreeze chemicals during installation or by rupturing of the ground loop coil. Once in the environment, many factors influence the fate of the chemicals. Table [1] lists some of the variables that may influence the mechanism of contaminant movement, retention and reaction (4).

In the absence of adequate corrosion rate information, the units have to be over designed to ensure reasonable life, however at the cost of extra resources and power. The indirect costs, due to change in appearance, damage to life and property, are quite minimal in this case. It, therefore, becomes necessary to generate corrosion data in environments resembling the real working climate, to understand the corrosion properties of any heat transfer fluid.

2. ETHANOL

Industrial ethanol is one of the largest volume organic chemicals used in industrial and chemical products (6). Ethanol has been used in U.S. to a considerable extent as an antifreeze (6). The production of ethanol from regenerable sources makes it

1. MOVEMENT OF CONTAMINANT THROUGH SUBSURFACE	
Parameter	**Variables**
Ground water flow rate	-formation permeability -time (eg. season) -depth
Subsurface permeability	-grain size and distribution -structural variability (eg. fractures)
Ground water direction	-depth -location (eg. recharge or discharge zone) -time (eg. season)
2. RETENTION OF CONTAMINANTS IN SUBSURFACE	
Soil/sediment absorption	-chemistry of subsurface formation -grain size, sorting, structure.
Microbial communities	-temperature -moisture -oxygen availability -nutrient availability
3. REACTION OF CONTAMINANT WITH SUBSURFACE MATERIALS AND BIOTA	
pH	-chemistry of subsurface formation -microbial activity
Redox status	-chemistry of subsurface formation -microbial activity -moisture -oxygen availability
Biodegradation	-temperature -moisture -oxygen availability -nutrient availability
Hydrolysis	-temperature -moisture

Table 1: Mechanisms influencing subsurface fate of contaminants

more attractive from the economic and environmental point of view. The manufacturing cost of ethanol is approximately 28.5 ¢/L, which is equivalent to a selling price of 60 ¢/L and the cost of denatured ethanol would be around 30 ¢/L (6). Since the emergence of ethanol as a key industrial raw material, chemical controls (denaturants that make ethanol unpalatable) have been administered by the government to prevent the tax-free ethanol from finding its way into beverages. The Tax-Free Industrial and Denatured Alcohol Act of 1906 was passed in the United States (6). The United States Treasury, Bureau of Alcohol, Tobacco and Firearms (BATF) now oversees the production, procurement and use of ethanol in the United States(6). Prevention of tax free industrial ethanol from finding its way into beverages calls for a combination of financial, administrative and chemical controls. Regulations establish four distinct classifications of industrial ethanol. The classifications with the most stringent financial and administrative controls call for little or no chemical denaturants. The classification that call for the most effective chemical denaturants require the least financial and administrative controls.

2.1 Physical Properties

Ethanol, (C_2H_5OH), under ordinary conditions, is a volatile, flammable, clear, colorless liquid. Pure ethanol has an ethereal odor. This compound burns with a non luminous flame, without soot, and forms carbon dioxide and water.(6,11). The hydroxyl group imparts polarity to the molecule and also gives rise to intermolecular hydrogen bonding. It is these two properties that account for the differences between the physical behavior of lower molecular weight alcohols and that of hydrocarbons of equivalent weight. Anhydrous alcohol is hygroscopic and absorbs moisture from the air. There is a volume contraction when ethanol is mixed with water and it reaches a maximum when one molecule of alcohol is mixed with three molecules of water, with evolution of heat (11).

Ethanol is an excellent solvent for many compounds (11). Gas solubility of oxygen is 25 vol. per 100 vol. of alcohol, 7 vol. of hydrogen, and 16 vol. of solubility for nitrogen in the same alcohol. The freezing point curve for aqueous solution of ethanol indicates its potential value as an antifreeze agent, Fig 1 provides a comparison of freezing point curves for aqueous solutions of methanol, ethanol and isopropanol(11).

A summary of physical properties (6) of ethanol are presented in Table [2]. The Material Safety Data Sheets (MSDS) of 200 proof ethanol and the denatured ethanol used for this study are given in the appendix.

2.2 CHEMICAL PROPERTIES

The chemistry of ethanol is largely that of the hydroxyl group, namely reactions of dehydration, dehydrogenation, oxidation and estrification (6). The hydrogen atom of the hydroxyl group can be replaced by an active metal, such as sodium, potassium, and calcium, to form a metal ethoxide with the evolution of hydrogen gas (6).

Aluminum and magnesium also react to form ethoxides but in the presence of mercury as a catalyst. Well cleaned aluminum filings react at room temperature in the presence of mercuric chloride (12,13). In an autoclave metallic aluminum and ethyl alcohol react without a catalyst at 120° C (14). The reaction can also be promoted by addition of sodium ethoxide (15). Ethanol behaves like water of crystallization and forms complexes with various inorganic compounds. The alcohol also combines with calcium, magnesium and platinum chlorides to form crystalline products(11).

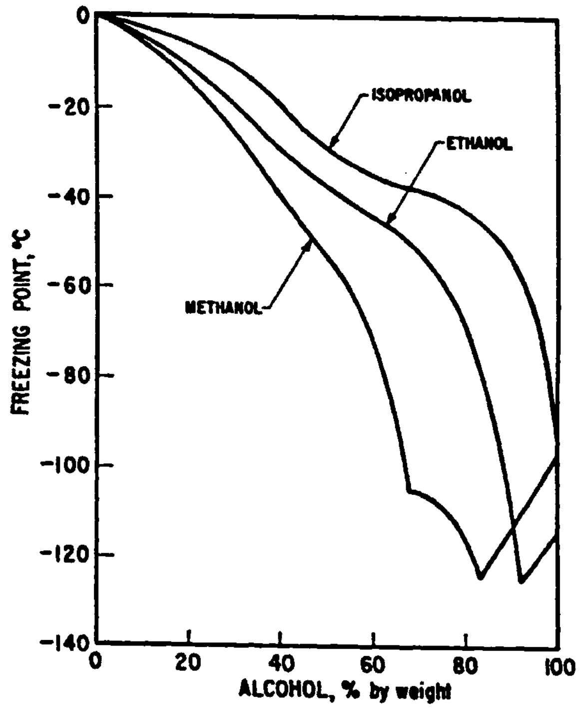

Fig 1: Freezing point curve for aqueous solutions of ethanol, methanol and isoproponal(11)

Property	Value
Freezing point, °C	-114.1
Normal boiling point, °C	78.32
Critical temperature, °C	243.1
Critical pressure, kPa	6383.48
Critical volume, L/mol	0.167
Density, g/mL	0.7893
Surface tension, at 25°C mN/m	23.1
Viscosity, at 20°C, mPa.s	1.17
Solubility in water, at 20°C	miscible
Heat of vaporization, at normal boiling point, J/g	839.31
Heat of combustion, at 25°C, J/g	29676.69
Heat of fusion, J/g	104.6
Flammable limits in air, vol%	
lower	4.3
upper	19.0
Auto ignition temperature, °C	423.0
Flash point, closed-cup, °C	14
Specific heat, at 20°C, J/g.°C	2.42
Thermal conductivity, at 20°C, W/(m.K)	0.170
Dipole moment, liq at 25°C, C.m	5.67×10^{-30}
Magnetic susceptibility at 20°C	0.734×10^{-6}
Dielectric constant at 20°C	25.7

Table 2: Physical properties of ethanol (11)

2.3 TOXICOLOGY AND SAFETY CONSIDERATIONS

Ethanol is a flammable liquid requiring a red label by the Department of Transportation (DOT) (17). Vapor concentrations between 3.3 and 19.0% by volume in air are explosive. Experience in industry indicates that ethanol is not a serious industrial poison. If proper ventilation of the work environment is maintained, there is a little likelihood that inhalation of the vapor will be hazardous. The threshold limit for ethanol vapor in air has been set at 1000ppm by the American Conference of Governmental Industrial Hygienists. At 350ppm the odor of ethanol can be barely identified(11).

Ethanol is oxidized completely to carbon dioxide and water in the body, thus it is not a cumulative poison(6). Ethanol, whether ingested or inhaled, inhibits the higher functions of the brain and then acts as an anesthetic. About 75-80gm of ingested alcohol will produce symptoms of intoxication in an average (70kg) person. About 150-200gm will cause stupor, and 250-500 gm may be a fatal dose(6). Repeated exposure to ethanol can lead to the development of a degree of tolerance, as measured by decreasing symptomatic reactions. Ingestion of ethanol does not damage the optic nerve as does methanol, but ocular functions - field of vision, depth, perception, visual acuity and eye coordination are affected adversely if more than 1 oz of whiskey per 30 Lb of body weight is imbibed (11).

2.4 ETHANOL AS AN ANTIFREEZE

The primary role of the circulating fluid in the heat pump is to transfer heat to or away from the earth. To provide efficient heat transfer, the antifreeze must have a high specific heat and thermal conductivity and low viscosity at operating temperatures. The efficiency of heat transfer is defined by the heat transfer coefficient (HTC). the higher the

HTC, the greater the efficiency of the system. The HTC is directly proportional to the thermal conductivity, the specific heat, and the density of the fluid and is inversely proportional to the viscosity, A slight penalty is incurred when an antifreeze is added to the aqueous heat transfer fluid. However, an antifreeze fluid is required to keep the equipment operational in subfreezing temperatures experienced during some part of the year.

Melinder and Granryd (16) in a study compared various heat transfer fluids as secondary refrigerants for heat pump systems based on, freezing point temperature, thermal conductivity, specific heat, density and viscosity, for various aqueous and non aqueous liquids. They found that, from a pure thermodynamic viewpoint calcium chloride, potassium carbonate and methanol would be best. The coefficient of heat transfer for calcium chloride and potassium carbonate is 25-100% higher than for other aqueous solutions. However, corrosion behavior, the environmental characteristics, flammability and toxicity have to be considered (16).

Though glycols are commonly used antifreeze solutions. they have been repudiated based on their high toxicity levels (17). Recently, it was recognized that acetates of calcium, magnesium and potassium possess the favorable combination of properties that are essential for any heat transfer fluid (8). In fact, potassium acetate has been widely used for deicing of runways in Europe(18). A comparison of ethanol-water, ethylene glycol-water and potassium acetate-water from the study of Melinder and Granryd (16) indicates the good potential of ethanol as an antifreeze.

The concentration required of ethanol to give a freezing point temperature of -15° C is 24.5%, where as that of potassium acetate is 23% and ethylene glycol is 30.5% Fig 1. The thermal conductivity of ethanol is 30% higher than potassium acetate over the whole temperature range of 30°C to -30° C. Ethylene glycol has a higher thermal

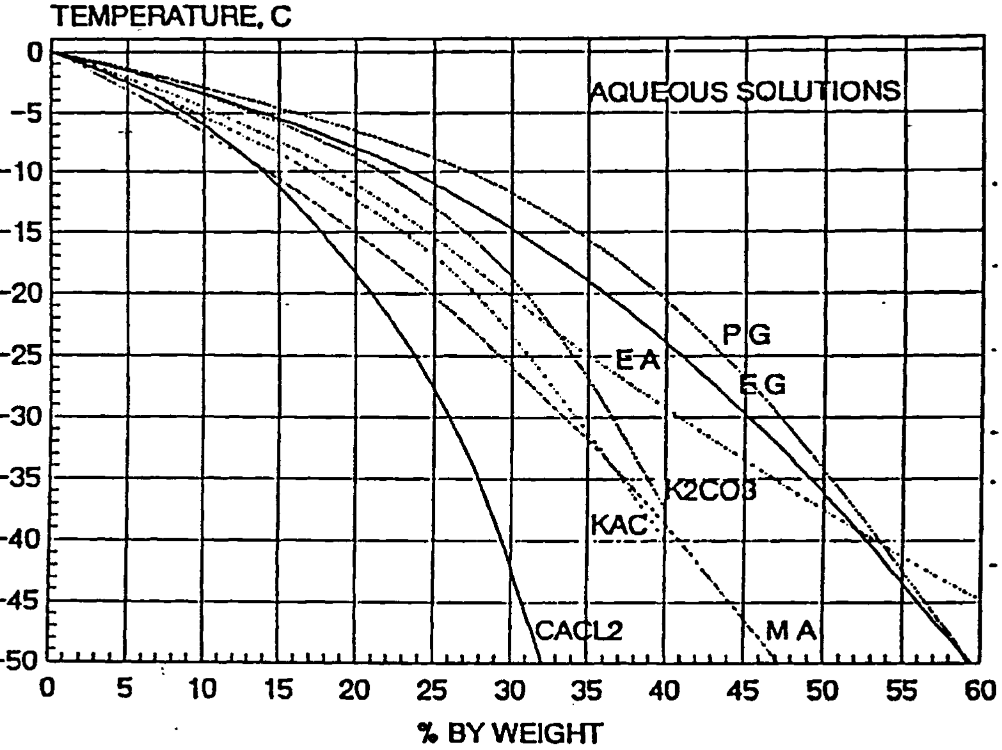

Fig 2: Freezing point curves of various aqueous and non aqueous secondary refrigerants for heat pumps(16)

conductivity at lower temperatures but the difference drops with increase in temperature (fig 2). Potassium acetate and ethylene glycol have lower values of viscosity than ethanol, however the dynamic viscosity of ethanol drops at a faster rate at a higher temperature.

The heat transfer coefficient F (α) is calculated as

$$\mathbf{F(\alpha)^{(15)} = 0.023 \times \lambda^{2/3} (\zeta . C_{\zeta})^{1/3} . \gamma^{1/3-0.8}}$$

Where, λ = Thermal conductivity (w/mk)

ζ = Density (kg/m^3)

C_ζ = Specific heat (J/kgK)

γ = Kinematic viscosity (m^2/s)

w = Flow velocity (m/s)

d = Tube diameter (m)

The F(α) for different fluids is given in Fig 3.

3. CORROSION AND ENVIRONMENTAL DETERIORATION IN METHANOLIC AND ETHANOLIC SOLUTIONS

With the production of alcohols from renewable energy sources becoming feasible and economical from the 70's, new uses for the lower alcohols are being discussed in several fields (19). Of the monohydric alcohol's, methanol and ethanol are being considered for various purposes, such as secondary energy carriers, additives to process streams in chemical industries and alternative vehicle fuels. Ethanol is being primarily considered to be used as an antifreeze in GSHP's, because of its favorable physical and chemical properties and environmental friendliness.

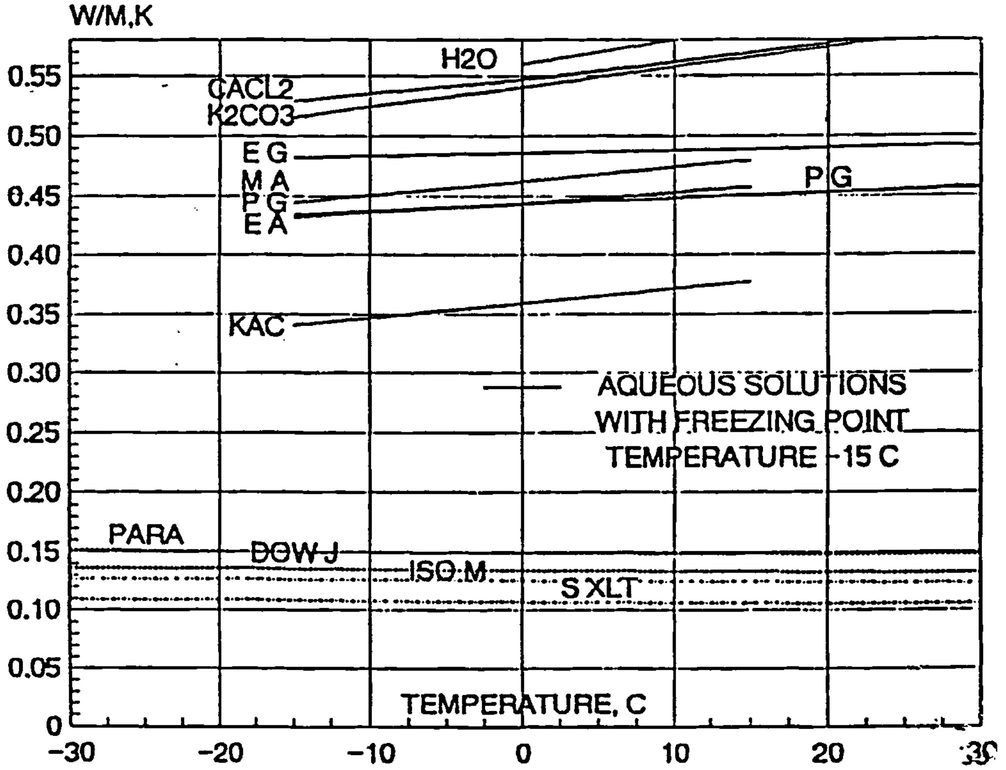

Fig 3: Thermal conductivity of various aqueous and non aqueous secondary refrigerants for heat pumps(16)

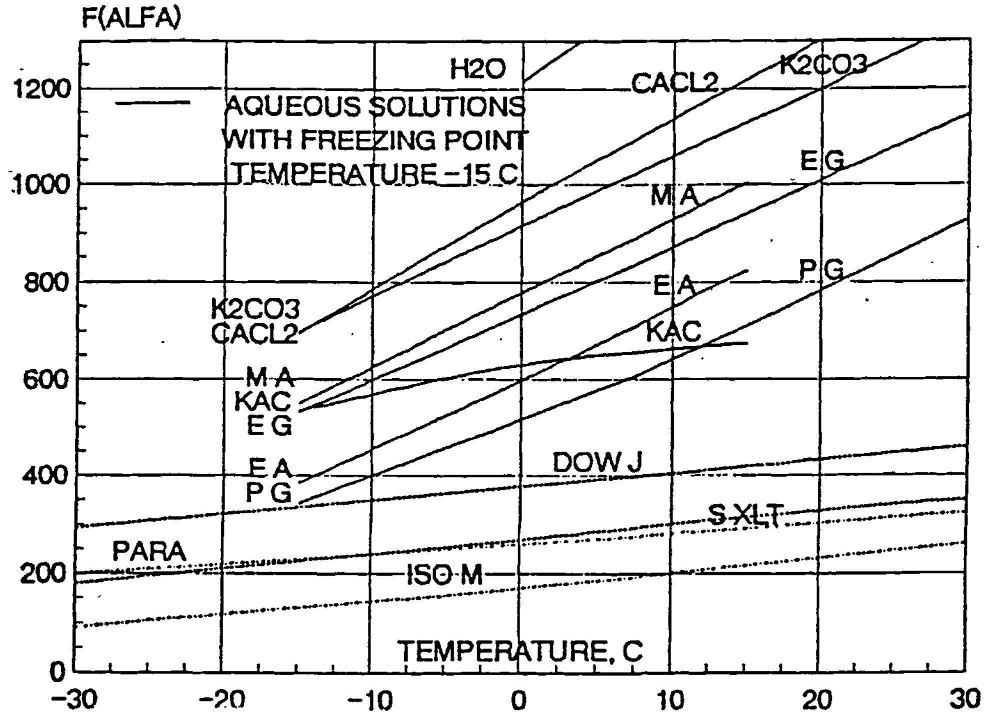

Fig 4: Property dependent factor for determining coefficient of heat transfer for various aqueous and non aqueous secondary refrigerants for heat pumps (16)

The corrosion processes in organic solvents are different from those in aqueous media (20). With monohydric alcohols emerging as the alternative fuels, several studies have been undertaken to evaluate the corrosivity of ethanol and methanol with various materials. The longer chain length of ethanol seems to provide resistance to corrosion compared to the shorter chain length of methanol, hence a comparison is drawn between these alcohols in most of the studies. Some practical methanol and ethanol fuels have been found to contain appreciable amounts of acid residues left behind by the production process.

A study conducted to investigate the compatibility of hydrated ethanol to different metals revealed that oxygen and carbon dioxide have an active participation in the corrosion process (21). Corrosion of tested materials Viz., zinc, aluminum, lead, tin was evaluated by mass loss, X-ray analysis of corrosion products and by pH, conductivity and acidity comparisons of solutions before and after testing (21). The presence of sulfates and acetates indicated that impurities present in ethanol were in part responsible for corrosion.

An elipsometric investigation of carbon steel corrosion in ethanol showed that carbon steel passivates in ethanol in both aerated and deareated solution; chloride additions led to pitting corrosion and may make the oxide more electrically conductive (22). Acid additions, except phosphoric acid, cause film dissolution followed by an oxide film growth. Nitric and sulfuric acid additions after an initial dissolution, followed by film growth, promote surface roughening, a process similar to the metallographic grain boundary etching, observed when etching solutions, such as nital, are used.

Anna (23) studied the effects of water and chloride ions on the electrochemical behavior of iron and 304L stainless steel in alcohols. It was found that iron passivates in all of the anhydrous alcohol media studied except methanol. The water concentration at the metal-solution interface differs from the bulk. In principle, solvent mixtures of alcohol and water behave such that the less water, like alcohols, show a stronger dependency on water concentration. In these instances, the diffusion of water to the metal solution interface is enhanced and therefore the passive film is more stable. On 304L stainless steel, additions of water have a passivating effect in HCl- containing alcohols independent of chain length. The anodic current density increased with an increase in water content for C2-C4 alcohols. For methanol the maximum occurred at a concentration of 0.5% H_2O, but at 1% H_2O, the current decreases and follows the trend of other alcohols.

The corrosion rates of zinc, iron and copper were observed in pure alcohols and in alcohol solutions of $HCOOH$, CH_3COOH, $HCOONa$, CH_3COONa (19). Higher acid strength seemed to increase the severity of corrosion. It was found that corrosion rates were higher in methanol than in ethanol. This was accounted for by the fact that longer aliphatic chain seems to afford corrosion protection. With the exception of Cu/CH_3OH, corrosion rates decreased with time.

Stress Corrosion Cracking (SCC) tests have been carried out in methanol and ethanol solutions to verify the different behavior of metals as a function of physico-chemical characteristics of the solvents, in particular dielectric constant and dipole moment (24). Tests carried out in organic solvents were done with lithium perchlorate as the supporting electrolyte. The choice of this supporting electrolyte was based on the assumption that the perchlorate ion, having a symmetric and low electric charge density, is characterized by a negligible complexing power and a low tendency to be absorbed on the metal surface. (24).Tests carried out in methanol and ethanol solutions containing 10^{-1} mol m^{-3} LiCl, 10^{-1} mol m^{-3} H_2SO_4, without a supporting electrolyte, gave well developed cracks on low alloy steel specimen. Stress corrosion cracks were developed on the specimens subjected to an ethanol solution containing 10^{-1} mol m^{-1} LiCl and 10^{2} mol $m^{-3}LiClO_4$.

The electrochemical behavior of austenitic 304 stainless steel in ethanol, isopropanal and t-butanol containing different concentrations of H_2SO_4 has been investigated by Singh et al (20). It was found that the critical current density for passivity depended on the concentration of the acid. The anodic critical current density increased as the acid concentration increased in ethanol. The shift in the corrosion potential may be explained in terms of dissolution of the air formed oxide that is formed at the time of immersion of the test specimen in the solution. The dissolution of the oxide is favored more and more as the acid content is increased, and the resulting surface assumes a more negative corrosion potential value. Scanning electron microscopy examination of the electrode surfaces after the polarization studies showed severe pitting of stainless steels in high concentration of acid in ethanol.

The dissolution and passivation kinetics of amorphous alloys with 10% chromium were investigated as a function of the water content in ethanol/water mixtures with 0.5N HCl, and compared to the behavior of the 304 stainless steel by Elsner et al (25). For 304 stainless steel, the same mechanisms were found to be effective both in aqueous and inorganic/water solutions. A stable passive film, consisting of hydrated chromium - oxy - hydroxide - is formed in the presence of sufficient amount of water. However, for the amorphous alloy Fe- 10Cr- 13B-7C, the fundamental passivation mechanism is the same but the formation of the BO_2^- leads to the formation of a membrane inhibitor on the surface, and reduces the critical current density for passivation, so , passivation is possible in organic solution with a lower water content.

Cavalcanti et al (26) studied the effect of water , sulfate and pH on the corrosion behavior of carbon steel in ethanolic solutions. No corrosion was noticed on the surface of the specimens exposed to non aqueous ethanol, whilst pits could be observed on specimens exposed to ethanol+ 10% v/o H_2O. With reference to ethanolic solutions containing 4.8% v/o H_2O, a few pits could be detected, when observed under an optical microscope at 50X magnification. As suggested by Heitz (27), the greater solubility of corrosion products in hydrated ethanol may account for such behavior. However, an opposite effect is observed in the case of more noble ferrous alloys, such as stainless steel, where H_2O in methanol and ethanol was found to enhance passivation and inhibit pitting corrosion (28, 29). A more recent investigation, utilizing infrared absorption spectrometry and X-ray diffraction, detected an amorphous film on the surface of carbon steel specimens immersed in 6% v/o water ethanol solution, in contrast with the observed presence of crystalline films developed at higher concentrations of water (30). Considering the greater corrosion resistance conferred by amorphous films in relation to crystalline films, the possible existence of an amorphous film on the surface of the specimen exposed to 4.8% v/o water ethanol solution may also account for the relatively low extent of corrosion verified in the latter case. No corrosion attack was found when the pH was maintained between 8 and 9, by the introduction of sodium hydroxide (26).

Szkolarka et al (28) investigated the pitting of stainless steel in water containing methanol. Pitting of stainless steel occurred in anhydrous CH_3OH and in that containing less than 8 moles H_2O/liter, but did not occur in solutions with higher contents, suggesting that H_2O increases the resistance of the passive film to localized breakdown. The aggressiveness of CH_3OH towards anodically polarized steel is probably caused by the formation of oxidation products of methanol. Oxidation of methanol leads to acidification of the solution, thereby increasing the corrosivity. The total oxidation process of methanol can be presented as

$$\mathbf{CH_3OH \ \text{--------}> CH_2O + 2H^+ + 2e^-}$$

$$CH_2O + H_2O \text{ --------->} HCOOH + 2H^+ + 2e^-$$

$$HCOOH \text{ ---------->} CO_2 + 2H^+ + 2e^-$$

Additional experiments have shown that the steel investigated also suffered pitting, when anodically polarized in other alcohols like ethanol and propanol (28).

Wear rates have been studied in high C- Cr steels (AISI 52100) in gasoline - ethanol - water (31). The variables were speed, load, temperature and water content in the gasohol. The highest wear rates of steel were found to be in gasohol with about 20% ethanol content. The wear was classified as corrosive wear, which is jointly effected by O_2 and H_2O. The main mechanism of metal loss was by mechanical adhesive wear(31).

Stainless steels, titanium and aluminum are representatives of alloys that develop a protective oxide or film on the surfaces exposed, and they appear to be more readily cracked in methanol-chloride solution than metals, with less protective films such as ordinary steels or brass (32). Investigations upon unnotched specimens of titanium and its commercial alloys revealed that at least 10-5N chloride is necessary for either SCC or any corrosive attack to occur (32). The oxide film is penetrated and the base metal is attacked whether stress is applied to annealed specimens or not (32). Sensitized 302 stainless steel was susceptible to attack by methanol containing chlorides, but no detectable damage occurred after 1000 hours in pure methanol (32). The two austenitic steels investigated, 302 and 321, were susceptible to attack by methanol containing 0.01N $FeCl_3$, in spite of a stabilized anneal (32). Neither alloy was attacked by methanol containing 0.01N NaCl after a stabilizing anneal, but the 302 alloy cracked when sensitized.

Persiantseva et al (33) studied the affect of aqueous ethanol on aluminum, copper and steel. The investigations were conducted in unmixed hydrolysis alcohol with different water contents, the specimens were completely immersed for 15 days. They found that the dependence of the corrosion rate of steel and copper on the water content had a maximum at 50% water. Water contents of more than 50% acted as a passivator for steel. It was assumed that at specific contents, water forms a protective film at points of damage. The complex dependence of the corrosion on the water content may be due to competing adsorption of the solution components and formation of various surface compounds.

Titanium alloys are subjected to SCC in methanol (34).A study by Scully and Powell (35), on the stress corrosion cracking mechanism of α-titanium alloys at room temperature, discusses the role of H in causing rapid transgranular SCC in relation to the hypothesis that H enters the unfilmed surface at the crack tip and causes slow strain rate embrittlement. It was found that the ratio of the activating to passivating species in the environment is important in promoting film formation and accounts for the protective effect of cathodic polarization. It is not effective in non film-forming conditions. Results in CCl_4 suggest that the residual water content (200ppm) is responsible for cracking. In a CH_3OH -HCl environment, the degree of embrittlement increases as the strain rate is lowered. Evidence for H embrittlement is provided by quantitative fractographic measurements of specimens anodically polarized in CH_3OH -HCl, on which the cleavage markings obtained upon subsequent fracture in air are not seen, if the dissolving front progresses at a rate comparable to H diffusion and by fractographic comparisons with broken hybrid specimens.

Sedriks and Green (36) studied the effect of additions of various metal ions to the to the environment on intergranular SCC and corrosion of unalloyed titanium in a methanol-HCl solution. Separate additions to the solution of palladium, gold iron, and copper ions in quantities ranging from 0.01 to 1000ppm, caused increase in both susceptibility to SCC and inter granular corrosion. Electrochemical studies established that this increase resulted from the enhancement of the overall cathodic process (36).

4.SUMMARY

The conclusions from the foregoing are that austenitic stainless steels and titanium are subjected to SCC in methanolic and ethanolic environments. Iron, stainless steel, zinc and copper are susceptible to pitting in methanolic and ethanolic environments. The longer aliphatic chain length of ethanol seemed to afford corrosion protection compared to methanol.

Stainless steels are subject to SCC in Methanol and ethanol in presence of chlorides. However, they are not susceptible in pure alcohols. The mode of cracking in SCC was intergranular.

Pitting propensity is proportional to the acid concentration in the solution. The critical current density for passivity depended on the concentration of the acid. The susceptibility to pitting is dependent on a critical v/o of water percent in the solution. This critical value may be different for different metal-solution systems. The susceptibility of pitting is effected by the pH of the solution. No corrosion is found to occur when pH is maintained approximately between 8 and 9.

CHAPTER III

EXPERIMENTAL PROCEDURE

1.MATERIALS

The materials investigated are gray cast iron, 304 stainless steel, yellow brass, copper, sealants, solders and rubber hoses. Gray cast iron has been chosen as it is known that it is more susceptible to corrosion than ductile iron. 316 austenitic steel being more noble it was presumed that if 304 stainless steel remains unaffected in the test environment so would 316 stainless steel. Similarly yellow brass with 30% zinc is more susceptible to attack in the form of dealloying than red brass. Polyethylene which is the ground loop material in GSHP systems was not tested as it was seen fron the review of literature that it is not subject to any form of attack by alcohols.

1.1 ETHANOLS:

Tests were conducted in the laboratory with 200 proof ethanol, a denatured ethanol (Aaper alcohol) and an inhibited commercial product "ENVIRONOL". The properties of the denatured ethanols are given in tables [3] and [4] respectively. The Material Safety Data Sheets (MSDS) are given in the appendix.

1.2 GRAY CAST IRON:

Gray cast iron (GCI) is used for housings of GSHP's. Cast iron is the preferred material due to its ready availability and low cost.

COMPOSITION

Component	Approx %
Ethanol	87
Methanol	5
Ethyl acetate	1
Methyl iso butyl ketone	1
Hydrocarbon solvent	1
water	5

COLOR : Clear colorless liquid

VAPOR DENSITY : 1.59

BOILING POINT : 79.4°C

FREEZING POINT : N/A

SPECIFIC GRAVITY : 0.81

SOLUBILITY IN WATER : Miscible

VAPOR PRESSURE : 40

FLASH POINT : 57°C

Table 3: Physical properties of denatured ethanol

COMPOSITION

Component	Approx %
Ethyl alcohol	89.14
D. I. Water	1.36
Sodium Meta bisulfite	0.06
Danatonium benzoate	0.0005
Isopropyl alcohol	0.18
Methylene blue	0.0006

COLOR : clear and light blue

VAPOR DENSITY : 1.59

BOILING POINT : 173° F

FREEZING POINT : -150° F

SPECIFIC GRAVITY : 0.80 @ 60° F

SOLUBILITY IN WATER : Substantial

VAPOR PRESSURE : 44.6 mm Hg at 60°F

FLASH POINT : 52°F

Table 4: Physical properties of "Environol"

GCI's are alloys of iron that contain 2.5 to 4% carbon and 1 to 3% silicon. They can be thought of as a composite of steel and flake graphite. Silicon is a graphitizer. It also promotes the formation of a strongly adherent surface film on cast iron, although considerable time may be required in some environments (37). As a consequence, the corrosion rate declines in most environments to a low steady state rate after the film formation.

A form of corrosion unique to GCI is the selective leaching attack, commonly referred to as graphitic corrosion. Graphitic corrosion is observed in GCI in relatively mild environments in which the selective leaching of iron leaves behind a loose network of graphite. This type of corrosion takes place because graphite establishes a galvanic cell with the iron matrix. The flake graphitic structure traps corrosion products and retards the corrosion rate. Graphitic corrosion occurs only when corrosion rates are low. When rates are high, the graphite is also removed and uniform corrosion occurs.

1.3 COPPER:

Copper is extensively used for piping in the heat pump systems. It is commonly used in the heat exchanger coils of the heat pumps. While copper is an essential constituent of GSHP systems, tests were not carried out in this study for the following reason. If yellow brass was not susceptible to corrosion in this environment than the more noble copper would not be. In a study conducted by Ngoh (17) using acetate based solutions copper did not show any potential for corrosion. SCC a common problem with copper alloys is practically unknown in commercial copper (38). Coppers resist corrosion under almost all conditions of service in alcohols (38).

1.4 BRASS:

Brass is found in the pressure and temperature sensing ports located in the inlet and outlet of the heat pumps. It is also widely used as fittings and pipe connectors.

Brasses are basically copper-zinc. Zinc improves the mechanical properties by solid solution strengthening and reduces the cost of alloy. Yellow brass (30% zinc) is the most common alloy. The potential corrosion issues with brass are SCC, dezincification and erosion corrosion.

SCC occurs in alloys with a static tensile stress in the presence of specific environmental conditions. For SCC, a passive surface film under oxidizing conditions must be present, and corrosion rates are consequently quite low. Brasses are susceptible to SCC in ammonia solutions.

Dezincification is a corrosion process in which selective dissolution of zinc, being the more active of the two, occurs in preference to the copper, and is common in chloride solutions. Removal of zinc leaves behind a porous mass of copper, which is readily recognizable by its reddish color. Dezincification, if not arrested, continues leading to penetration and unexpected failure. Where dezincification may be a problem, red brasses (zinc < 15%) are used, for they are practically immune (9).

1.5 STAINLESS STEEL:

Many circulator pump interior components are made of stainless steel, for example the rotor and impeller. They are typically cold worked items and may have residual stresses. Also, the impeller may have spot welds. For some pump models, the pump housing is made of stainless steel.

Iron based alloys containing at least 10.5% chromium are called stainless steels. The austenitic stainless steels to which type 304 belongs, are widely used in industry. The addition of nickel to iron-chromium alloys stabilizes the face-centered cubic (FCC) austenitic phase and improves corrosion resistance synergistically with chromium. FCC stainless steels are identified easily, because they are not magnetic. Stainless steels derive their corrosion resistance from a thin hydrated, oxidized, chromium-rich, passive surface layer. SCC, pitting and crevice corrosion are the potential corrosion problems that could arise due to the breakdown of passive layer. Metallurgical segregation, causing localized depletion of chromium, can result in passive breakdown at grain boundaries and inter granular corrosion. This can often happen in welding and terms such as weld decay and sensitization are descriptive (9).

1.6 SOLDERS:

Lead - tin solders find extensive use in joining the copper piping of the heat pumps. Solders are traditionally lead - tin alloys. Recently, there has been an effort to develop lead free solders because of the Federal Hazardous Substances Act passed in 1986 (39). This act restricted the maximum lead content of the solders used in potable water systems to be not more than 0.2%. Some special purpose solders, like 95% tin/5% antimony solder, and tin/silver solders, have been in use prior to the ban on lead. However, their use was restricted by high cost (39).

With the concern about lead solders, a host of new lead free solders have been introduced. One of the earlier solders is the generic 95% tin/5% antimony solder which is widely used in joining copper alloys in heating systems. Like 95/5, tin/silver solders have been in use prior to the ban on lead in refrigeration lines. Silverbrite 100, the tin-based 4.5% copper, 0.5% silver alloy; Bridget, containing 5% antimony, 3.5% copper and 0.275% silver; AquaClean containing 0.2 0.5% silver, 0.20% copper and 3.25% bismuth were the first of the new silver based solders to be introduced(39). Because of their relative high cost, however, the tin/silver solders have not been used too much on hardware involving potable water systems. The tin/silver solder outperformed the conventional tin/lead solder in rupture tests and stress rupture tests. According to metallurgists at Fry Metals choosing a lead free solder which has a melting range similar to that of a lead-based solder may be the quickest way to reach a decision, but other factors, such as cost, corrosion behaviour, joint strength, service temperature, flux, process and availability also have to be considered (39).

For an understanding of the corrosion behavior of the solders, two features must be taken into consideration. Firstly, fluxes are usually used, and, secondly, the solder exposure areas are much smaller than the area of the materials being joined.

Fluxes, function as oxide removers and may contain hygroscopic products that, if not removed, will promote corrosion. Some powerful fluxes contain as additives, chlorides, bromides, H_3PO_4 and mixtures of these (40). Residues from such fluxes must be removed as completely as possible, by either mechanical wiping or with solvents. However, right design with the formation of protective corrosion products over the joints, permits the satisfactory use of the soldered joints in conditions that may appear hostile at first.

The overall corrosion behavior of solders will be similar to that of the predominant metal. In most cases, the presence of lead forms many insoluble deposits, for example oxides and sulfates, which prevent further corrosion. Volatile organic acids, such as acetic acid, attack lead containing solders and produce a white encrustation and cause severe destruction of the metal. Where such attack occurs, substitution with a higher tin content has been suggested (40).

Solders, even though being anodic to copper, have been widely used without trouble in conventional commercial and domestic plumbing. But, under adverse conditions, lead is selectively leached from the commonly used 50 tin 50 lead plumbing solders into the system, which has caused concern about lead poisoning.

Pure tin, on the other hand, may be dissolved by alkalis with the production of soluble stannates or stannites. Any surface oxides will be dissolved in solutions with pH >12 and sometimes with a pH of 10 and corrosion will follow. When corrosion is possible, the corrosion rate is governed by the temperature and the rate of arrival or any oxidizer to the initial surface, and is not greatly affected by the character of the alkali in long periods of immersion.

1.7 ELASTOMERS:

Elastomers are used to connect the water source heat pumps to the main supply headers or the circulator pumps.

The most outstanding characteristic of rubber and elastomers is resilience or low modulus of elasticity. Flexibility accounts, for the most part, its use in tubing. Organically, rubbers are long chained molecules and are usually soft by nature. This problem is overcome by what is known as "Vulcanization" or simple stated, adding sulfur and heating to enhance the bonding between the molecular chains or cross linking. Commonly rubbers deteriorate by physical or chemical means or both. Physical means, include swelling by absorption water and chemical disintegration occurs due to failure of bonding between the molecular chains (41). It is important to note that rubers are usually polar, based on isopropene or butadeine, but polar rubbers are needed to resist swelling by non polar gasoline and vice versa.

1.8 SEALANTS:

Sealants are normally used as fillers for joints and for binding building materials. In the heat pump systems, sealants are used at the piping joints. Several types of sealants are available in the market for this purpose. Sealants are classified broadly as silicones, urethanes, polysulfides, halogenated butyl rubber etc., based on the binders used. In the present study an effort has been made to classify the different sealants used based on the composition available from the Material Safety Data Sheets and data obtained from the technical information services of the manufacturers. The sealants are classified and tabulated with their physical properties in table [5].

The sealants are elastomeric products, which cover a wide range of elasticities and cold flows, and as such they are ideal for filling joints. They can deform under stress to such a degree that the contraction and expansion of the rigid structure can be easily absorbed without destroying the bonds. Because of their cushioning and damping properties, they can change industrial techniques and building practices (42). When cured, they bind the structural materials and are able to expand or contract with the motion of the connected elements. They also form a tight barrier against moisture, gases and chemicals. On curing the sealants may harden or remain tacky (42)

1.9 INHIBITORS:

Inhibitors, in critical quantities, reduce the corrosivity of the environment. In heat pump systems inhibitors are circulated along with the heat transfer fluid.

A corrosion inhibitor may work by forming a protective coating, in situ, by reaction of the solution with the corroding surface. (10). In another sense, it is a corrosion retarding catalyst. Alternatively, inhibitors may work by removing an active species (eg. oxygen) from the system. A corrosion inhibitor must be effective at low concentrations, broad range of pH, working temperature and must have minimum toxicological effects when discharged. (42).

Most inhibitors used in corrosion control are proprietary and hence specific information is lacking. A study conducted by Nayak (8) on GS-4, a potassium acetate based antifreeze solution, indicated high levels of phosphorus and silicon in the EDX

Name of Sealant	Classification	Color and Appearance	Vapor density	Boiling Point	Vapor Pressure	Specific Gravity	Solubility in water	Flash Point
Real Tuff	Isopropanol based	White thixotropic paste	N/A	N/A	N/A	1.56	Insoluble	N/A
Harvey's Seal	Isopropanol based	Yellow-tan Paste	N/A	173°F	N/A	1.36	Slight	70°F
Gripp	Isopropanol based	Dark brownish black paste	2.07	180°F	33 at 20°C	1.29	Insoluble	53°C
LA-CO Slick	Silicone sealant	White paste	N/A	350°F	1	1.42	Insoluble	300°F
ZEP Pipe Seal	Isopropanol based	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Teflon Paste	Isopropanol with TFE	White paste	1	173°F	N/A	1.41	Slight	70°F
Permatex	Isopropanol based	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Jomar-green	Isopropanol based	Green paste	>1	180°F	0.88 at 25°C	1.41	Slight	70°F
Hercules Block	Isopropanol based	N/A	N/A	N/A	N/A	N/A	N/A	N/A
HVAC Permatex	Acrylic sealant	Blue paste	N/A	212°F	N/A	1.7	Water based	None
Pro-dope	Isopropanol based	Gray paste	N/A	N/A	N/A	1.61	Insoluble	N/A
LA-CO Anaerobic	Isopropanol based	White paste	N/A	300°C	10mmHg at 80°F	1.21	Slight	>200°F

Table 5: Classification of sealants and their physical properties.

analysis, indicating the probability of phosphate, polyphosphate or a phophonate and may be silicate or combination of these, like potassium silicate and tri-potassium phosphate. Typically phosphates and silicates are used as inhibitors in heat pump systems along with an organic film former.

Inhibitors can be broadly classified as anodic, cathodic or mixed mode inhibitors according to the rate process being controlled. Anodic inhibitors suppress the anodic or the oxidation reactions; likewise, cathodic inhibitors impede the cathodic reaction, and the mixed mode hinders both.

Phosphates are anodic inhibitors and are effective in the presence of oxygen (43). The protective properties are a function of pH. The use of phosphate as an inhibitor is relegated to mostly alkaline environments ($pH>8$). At low concentrations (few mg/liter), the phosphate ions will cause pitting attack (44). The oxygen content of the system is primarily responsible for the ability to inhibit corrosion of the steels by phosphates. Oxygen in the system produces a thin film of Fe_2O_3 and the phosphate ions help in accelerating the film formation, which restrict further diffusion of Fe^{2+} ions to the surface. The presence of aggressive chlorine ions can cause film breakdown and pitting attack takes place. The repair of the film will depend on $(PO_4)^{3-}$ level and oxygen concentration. Also, the overall inhibition by the phosphate ion is sensitive to water quality and pH. With high calcium hardness of water, the potential for calcium phosphate deposition increases with water hardness, phosphate level, pH and temperature. Sometimes this can simulate under deposit corrosion.

Polyphosphates are cathodic inhibitors. Different kinds of polyphosphates are available for use as inhibitors. Orthophosphates, used either as mono, di or tri metal salts, are mostly suggested for use in alkaline environments (43). In case of polyphosphates, calcium ions are needed for effective inhibition of steels, as it promotes the film formation.

Phosphates protect ferrous materials through a mixed mode of inhibition and differ from polyphosphates by the direct bond formation between the phosphorus and carbon atoms, instead of the phosphorus-oxygen bond. They are good especially at high pH values. Locally, incipient attack occurs initially but is rapidly arrested. However, Cl^{-4} ions degrade the inhibitors. Phosphonates are good for non-ferrous alloys but this can be overcome by addition of zinc.

Silicates, another group of inhibitors, are used in heating and cooling systems frequently. These are again available as metal salts with varying degrees of silicate polymerization. The silicates are stable only at high pH levels and readily form insoluble slats with water hardness formers. These precipitates are highly abrasive and can also form high thermal insulating layers on the heat exchangers. They, however, are useful in neutralizing the effects of acid soft cuprosolvent waters and to minimize dezincification.

2. SPECIMEN PREPARATION

2.1 Cylindrical Specimens:

Cylindrical metal specimens were cut from bar stock, using a cut off wheel. The specimens were approximately 12.7mm in diameter and 12.7 mm in height. They were ground to a 240 grit finish to simulate a machined surface. Some specimens were ground through 600 grit abrasive paper and polished 5μm alumina, in order to get a mirror finish. Stainless steel and brass specimens were then indented using a 10mm ball indentor to induce residual stresses, so as to may be induce stress corrosion cracking subsequently. The specimens were cleaned and degreased by rinsing in water and water free absolute 200 proof ethanol and then dried using hot air blowers.

2.2 Wedge opening loading (WOL):

The slow bend version of the WOL specimen was made based on a schematic given for the self loaded configuration for a wedge opening loading specimen. The specimen was bolt loaded to constant displacement at $K_1 > K_{1scc}$. The dimensions of the specimen were 25mm x 25mm x 12.7mm. The V notch was rough machined to an angle of 40± 2°.

2.3 Sealants:

The sealants were tested using 25mm long couplings of low carbon steel with threaded ends closed with hexagonal galvanized/brass fittings. The cylinders were filled with the test solution and the threaded ends tightened using the sealants under test.

3. TEST PROCEDURE

3.1 IMMERSION TESTS:

The test procedures used the ASTM G31-72 specifications as a guideline (45). It describes the standard practice for the laboratory immersion testing of metals. In designing these tests, for the simulation of corrosion of heat pumps in the laboratory, factors that are encountered in practice were taken into consideration, so as to emulate the purpose of the tests. For immersion tests, the volume of the solution used was calculated as 125 ml/in of metal exposed (45). Due to the evaporative nature of the solutions at the test temperatures, composition was controlled by the periodic addition of solution to maintain the necessary volume within ±2%. The test beakers were filled with solution covered with Saran Wrap, a commercial poly vinylidene chloride plastic film that has barrier properties, secured with rubber band and then covered with Aluminum foil to minimize evaporation losses, minimize oxygen pickup and avoid contamination of the test solution. The tests were carried out (in a fume hood) at 50° C, using a hot plate. This temperature was selected as it was slightly above the highest temperature anticipated with a heat pump system in service. The solutions were saturated with air, whenever necessary, by bubbling air for about 3 minutes through the solution on a daily basis. The testing conditions were controlled throughout the tests in order to ensure reproducibility of results. For studying the effects of dilution with water, a 50 % v/o solution were used in the tests as it was seen from the review of literature that corrosion rates had the strogest dependancy on water content at 50 v/o..

The metal specimens were then taken out of the solution and rinsed according to the chemical procedure given in the ASTM specification G1-A1 (45), dried and weighed every week. Changes in surface conditions were monitored by observing under a stereoscopic zoom microscope. Also, visual changes in the test solutions were recorded for each test conducted. The corrosion rate was calculated in mils per year (1mil = 1/1000 in) wherever applicable by using the equation (9).

$$\mathbf{MPY = (534\,W)/\,DAT}$$

where,

MPY - Corrosion rate in mils per year
W - Weight loss in milligrams
D - Density in grams per cubic Cm
A - Area exposed in square inches
T - Time of testing in hr.

3.2 METALLOGRAPHY:

For evaluation of pitting corrosion, specimens were chemically cleaned to remove corrosion products (45). Gray cast iron was cleaned in a solution of 200 g sodium hydroxide (NaOH), 20 g zinc chips and reagent water to make 1000 ml for about 30 minutes at a temperature of 80 C. Brass specimens were cleaned in a solution of 500ml hydrochloric acid (HCl) and 500 ml water. Type 304 stainless steel specimens were cleaned in a solution of 100 ml nitric acid (HNO_3 Sp gr 1.42) and 900 ml reagent water.

The pit density was determined by counting the number of pits through a microscope eyepiece by using a paper grid containing 30° V notch placed on the metal surface. The pits were counted in each gap, and the grid was moved symmetrically until all the surface has been covered (45).

To evaluate the extent of pitting and compare with standard rating charts for pits, a microscopical method was used, as the pits were difficult to penetrate with a probe type of instrument. A single pit was located on the metal surface and centered under the objective lens of the microscope at low magnification. The objective lens magnification was increased until the pit area covered most of the field under view. The lip of the pit was first brought under focus, using first the coarse and then the fine focusing knob. The initial reading was noted from the fine focusing knob. Then, the bottom of the pit was brought into focus and the reading on the fine focus knob noted. The difference between the initial and the final reading gave the pit depth (45). Metal penetration was then expressed in terms of pitting factor, which is the ratio of the deepest metal penetration to average metal penetration.

The WOL specimen is shown in fig 5 . The modified form of slow bend version of WOL specimen is shown in fig 6 . In this type of specimen one of the loading pins is replaced by a threaded bolt, which permits self loading. The specimen used for tests is given in figure 7. The specimen was bolt loaded to constant displacement at $K_1 > K_{1scc}$ and exposed to corrosive solution.

3.3 Sealant Tests:

Recognizing that temperature cycling occurs in GSHP's, the sealants were subjected to test environment at 50°C, 80°C and to a freeze thaw cycle, where the sealant test specimens where alternately exposed to 80°C and -5°C every 24 hours over a periods of 6 weeks. These temperatures were chosen to exceed temperature variations in a heat pump system. A heat pump experiences typically a temperature cycle from 0- 50°C. Immersion tests were conducted on sealants, as sealant adhesion is nearly always adversely by water immersion. The U. S. Bureau of Reclamation states that " the single most deteriorating influence on the bond of elastomeric sealants is continuous water submergence (46). The sealants were graded based on leakage over a period of 6 weeks. Observations were made of solution color change and leakage. Apart from these, tests were also done to measure the time taken by the various sealants under study to harden completely by exposing them on a sheet of aluminum foil. The solutions were graded as hard or tacky after a period of 2 weeks.

3.4 SOLDERS:

Tin-Lead solders with compositions of 40-60 tin/lead, 50-50 tin/lead. 60-40 tin/lead, 70-30 tin/lead, 90-10 tin/lead were subjected to immersion tests. Besides the sealants made in the laboratory, tests were also conducted on commercial sealants with flux. Tests were also conducted on two lead free solders whose composition was 95 tin/5 antimony and 95 tin/5 silver. The solders were made in the laboratory in the form of small cylinders approximately 12.7mm in height and 12.7mm in diameter. Observations were for any leaching, attack or deposition.

3.5 HOSES:

In the case of the tests for rubber hoses, about 12.7mm length of hose material was cut from the three different hose samples provided and were subjected to immersion tests as per ASTM D471 specification. Three commercial hose materials were subjected to tests

1. Red rubber hose
2. Yeoman hose
3. Wildfire hose.

Observations were made to note any change in texture, swelling or feel of the specimen and any change in the color of the test solution.

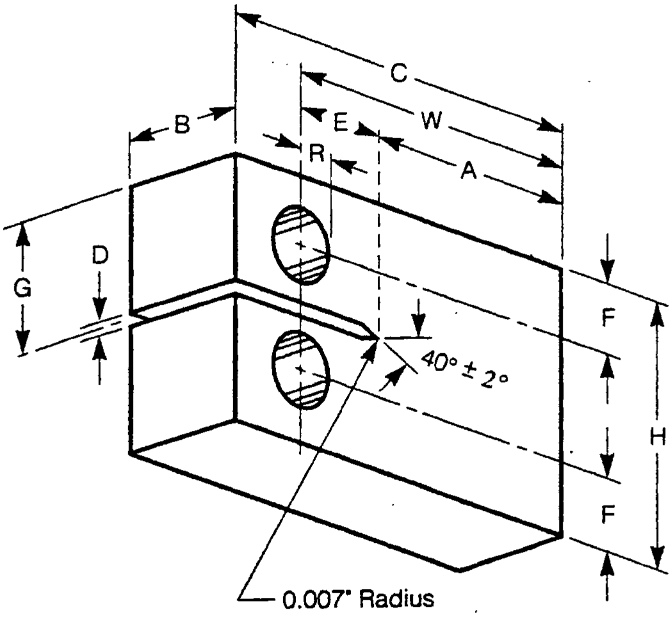

Fig 5: A schematic of WOL specimen with dimensions

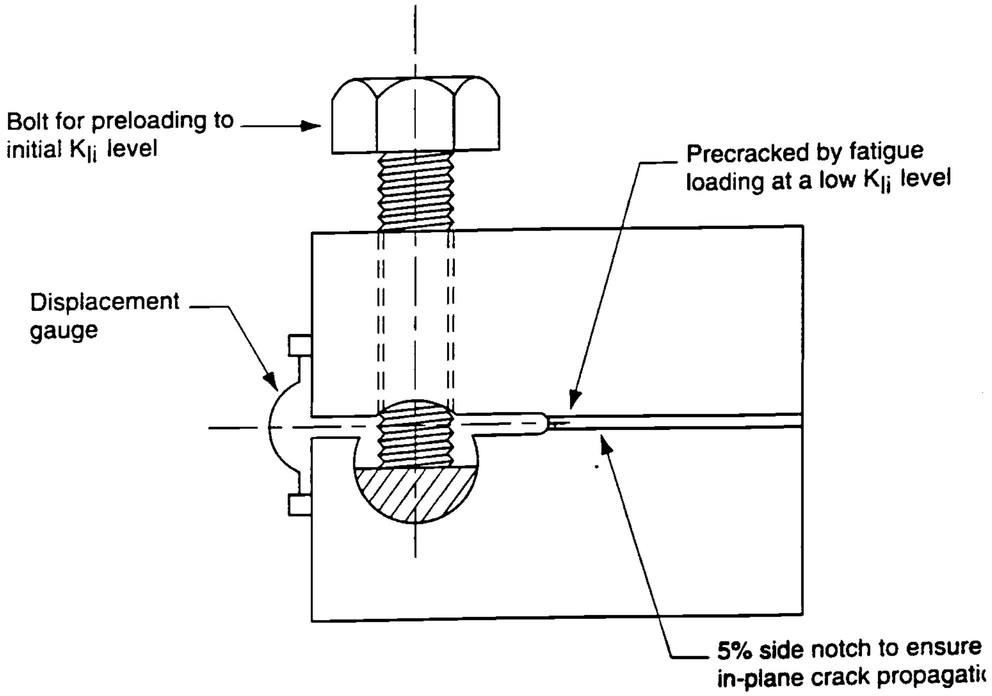

Fig 6: A modified form of slow bend version of WOL specimen

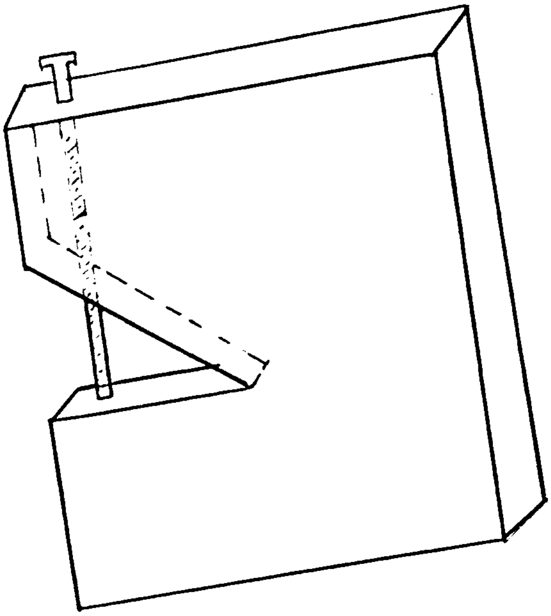

Fig 7.: Slow bend version of the WOL specimen used in the tests.

CHAPTER IV

RESULTS

1. METALS

1.1 ABSOLUTE ETHANOL

Gray Cast Iron: The attack on GCI was minimal. There was some etching on the top surface with a reddish brown deposition and pitting on the crevice side. The corrosion rate increased with air saturation, table 11. As can be seen from table 11 and 12 the effect of surface finish was negligible. Microscopic evaluation of deepest and average metal penetration revealed uniform corrosion with a pitting factor close to 1, table 13. However, pit density was the highest, table 14.

Stainless steel and Brass: The attack on brass and stainless steel was minimal with no significant attack in the form of pitting except slight staining of the brass specimen.

The WOL specimens did not develop any crack in both aerated and non aerated solutions

1.2 DILUTE ABSOLUTE ETHANOL

Gray Cast Iron: As was expected from the literature survey, dilution with water increased the corrosion rate of GCI in diluted absolute ethanol. The corrosion rate increased with air saturation, with affects of surface finish being negligible. However, the attack could be termed uniform general corrosion as there was general roughening of the surface pit dimensions could not be measured even under a magnification of 375X

.

Stainless Steel and Brass: There was no attack on either stainless steel or brass. There was a slight staining of the specimens on the outer edge of the bottom face. The WOL specimens remained unaffected in both aerated and non aerated solutions.

1.3 DENATURED ETHANOL

Gray Cast Iron: Pitting on both surfaces of the specimen was visible to the unaided eye. There was a reddish brown deposition on the crevice side. Aeration of the solution increased the corrosion rate, table 11. The effect of surface finish was negligible. A pitting factor of 1 in case of aerated solution suggests uniform corrosion. The pit densities however vary by a factor of 2.5 from aerated to non aerated solutions, table 14.

Stainless Steel and Brass: There was a slight staining of the stainless steel specimen. There was a reddish brown deposite on the outer edge of the crevice side of brass specimen. Brass was prone to crevice corrosion and pitting. However, the attack was minimal.

The WOL specimen of stainless steel developed a unbranched crack with a sharp lip at the notch root on the ninth day. There was no evidence of crack growth on subsequent examination. The brass specimen remained unaffected.

1.4 DILUTE DENATURED ETHANOL

Gray Cast Iron: The corrosion rate of GCI was highest in aerated denatured ethanol in terms of MPY, table 11. On visual observation, the specimen in non aerated solution seemed the most affected, with blackish brown deposits all over the surface. However, on chemically cleaning the specimen it was observed that the surface was less affected than the specimen in the aerated solution. Though aeration seemed to subdue metal penetration, table 13, it enhanced the corrosion rate in MPY, table 11. The pitting was more uniform in non aerated solution as can seen from the pitting factor, table 13.

Stainless Steel and Brass: There was no attack on brass or stainless steel in both the cases of the cylindrical and WOL specimens.

1.5 COMMERCIAL DENATURED ETHANOL

Gray cast iron: The corrosion rate was minimal and in the form of pitting. There was no measurable weight loss. Aeration did not have any effect on the corrosion rate. There aws some crevice corrosion on the bottom surface of the specimen. Microscopic examination showed traces of pitting.

Stainless steel and Brass: There was no attack of any kind on stainless steel. There was a white precipitate deposition on the sides and top surface of the brass specimen. The WOL specimens did not show any traces of a crack, for an immersion test period of four weeks.

2. SEALANTS

Sealant tests were evaluated on the basis of leakage, solution color change and state of hardness. "HVAC Permatex " though hardened on exposure to air in two weeks showed considerable leakage in the immersion tests. The test solution color changed to bright yellow. The commercial denatured ethanol changed to colorless from light blue. There was a white deposition on the bottom of the beaker. "Jomar-green" and "pro-dope" hardened on exposure, besides being leak resistant in the test environment. The test solution remained clear. A summary of the sealant test results is given in table 14.

3. ELASTOMERS

Of the three elastomers tested there was no attack observed in any of the solutions. There was a solution color change in all the cases. The red rubber hose softened to touch in the dilute denatured ethanol. There was no swelling or change in texture in any of the test specimens which is characteristic of some elastomers in alcohols.

ABSOLUTE ETHANOL

Test type : Laboratory immersion
Specimen : cylindrical
Temperature : 50° C ± 2°C
Condition : a) As poured, aerated.
b) As poured, non aerated
Time : 4 weeks

1. Material : **Gray cast iron**
Results : a) Reddish brown deposits on crevice side. Pitting visible under the microscope at 10X. No cracks were observed.
b) Muddy brown deposit on crevice side of specimen. Traces of pitting visible under the microscope

2. Material : **Stainless steel**
Results : a) No traces of corrosion, staining or etching of the specimen.
b) No corrosion was observed on the specimen except loss of brightness

3. Material : **Brass**
Results : a) There was no significant corrosion or pitting except for slight staining of the specimen.
b) There was a slight staining of the specimen.

4. Material : **Elastomers**
Results : a) No softening or swelling was observed but a solution color changed to brwon in case of Yeoman and Wildfire and yellow in case of Red rubber
b) The results were the same as in aerated solution.

Table 5: Summary of immersion test results

DILUTE ABSOLUTE ETHANOL

Test type : Laboratory immersion
Specimen : cylindrical
Temperature : 50° C ± 2°C
Condition : a) As poured, aerated.
b) As poured, non aerated
Time : 4 weeks

1. Material : **Gray cast iron**
Results : a) Reddish brown deposits on crevice side. Pitting visible under zoom microscope. Solution color changed to light brown.
b) Results were the same as in aerated solution.

2. Material : **Stainless steel**
Results : a) Slight staining of the specimen at the edges.
b) Same as above.

3. Material : **Brass**
Results : a) There was no significant corrosion except slight staining of the specimen.
b) Same as above.

4. Material : **Elastomers**
Results : a) The results were the same as in absolute ethanol.
b) Same as Above.

Table 6: Summary of immersion test results

DENATURED ETHANOL (CHEMICAL GRADE)

Test type : Laboratory immersion
Specimen : cylindrical
Temperature : 50° C ± 2°C
Condition : a) As poured, aerated.
b) As poured, non aerated
Time : 4 weeks

1. Material : **Gray cast iron**
Results : a) Reddish brown deposits on the crevice side. Pitting visible to unaided eye from 24th day. Rough surfaces on crevice side and top. Microscopic examination revealed pitting on both sides
b) Deposition was lesser compared to the specimen in aerated solution.

2. Material : **Stainless steel**
Results : a) Slight staining of the specimen at the edges. Evaporation was high when compared to beakers containing other specimens. The WOL specimen immersed in this solution developed an unbranched crack with a sharp lip at the notch root.
b) Slight staining of the specimen at the edges.

3. Material : **Brass**
Results : a)There were traces of crevice corrosion and slight deposition at the edges of the crevice side.
b) Same as above.

4. Material : **Elastomers**
Results : a) The results were the same as in absolute ethanol
b) Same as in aerated solution.

Table 7: Summary of immersion test results.

DILUTE DENATURED ETHANOL

Test type : Laboratory immersion
Specimen : cylindrical
Temperature : 50° C ± 2°C
Condition : a) As poured, aerated.
b) As poured, non aerated
Time : 4 weeks

1\. Material : **Gray cast iron**
Results : a) Black brown deposition all over the specimen decreasing progressively towards the crevice side. Solution color changed to muddy brown.
b) Brown deposition all over the specimen. Solution color changed to muddy brown. Microscopic examination after chemical cleaning revealed severe pitting comapred to the specimen in aerated solution

2\. Material : **Stainless steel**
Results : a) Slight staining of the specimen at the edges. Evaporation was high when compared to beakers containing other specimens.
b) Slight stainign of the specimen. The surfaces lost their lusture.

3\. Material : **Brass**
Results : a) There was no significant corrosion except for white deposition on the outer edge of the top surface.
b) Same as above.

4\. Material : **Elastomers**
Results : a) The results were the same as in absolute ethanol
b) Same as above.

Table 8: Summary of immersion test results.

COMMERCIAL DENATURED ETHANOL (ENVIRONOL)

Test type : Laboratory immersion
Specimen : cylindrical
Temperature : 50° C ± 2°C
Condition : a) As poured, aerated.
b) As poured, non aerated
Time : 4 weeks

1. Material : **Gray cast iron**
Results : a) There was no attack on the exposed surfaces. There was a brown deposition on the crevice side of the specimen.
b) The results were the same as in aerated solution. There was a white precipitate deposition at the bottom of the beaker.

2. Material : **Stainless steel**
Results : a) There was no attack even in the form staining or etching.
b) White deposition at the bottom of the beaker.

3. Material : **Brass**
Results : a) There was no attack however there was a white deposition on the sides and top surface.
b) Same as above.

Table 9: Summary of immersion test results.

MIRROR FINISH (600 Grit); AERATED

Weeks	Pure ethanol	Pure ethanol diluted	Pure denatured ethanol	Denatured diluted ethanol
1	0.0262	0.0364	0.0326	0.0421
2	0.0842	0.0542	0.0621	0.0986
3	0.0962	0.1863	0.0842	0.1824
4	0.1555	0.2068	0.1938	0.2639
MPY after 4 weeks	1.3	1.8	1.7	2.3
NON-AERATED				
1	0.0086	0.0163	0.0214	0.0312
2	0.0642	0.0698	0.0748	0.0643
3	0.0932	0.0945	0.0961	0.0988
4	0.1006	0.1320	0.1322	0.1321
MPY after 4 weeks	0.9	1.1	1.1	1.1

Table 11: Weight loss measurements for GCI (600 grit finish) in aerated and non aerated solution

MACHINE SURFACE FINISH (240 Grit); AERATED

Weeks	Pure ethanol	Pure ethanol diluted	Pure denatured ethanol	diluted denatured ethanol
1	0.0243	0.0298	0.0294	0.0361
2	0.0756	0.0496	0.0432	0.0598
3	0.0842	0.1823	0.0769	0.1968
4	0.1436	0.2004	0.1842	0.2582
MPY after 4 weeks	1.2	1.7	1.6	2.2
NON-AERATED				
1	0.0084	0.0042	0.0067	0.0018
2	0.0583	0.0592	0.0438	0.0354
3	0.0863	0.0763	0.0842	0.0842
4	0.0985	0.0926	0.1082	0.1127
MPY after 4 weeks	0.85	0.79	0.93	0.97

Table 12: Weight loss measurements for GCI (240 grit finish) in aerated and non aerated solutions

Material: Gray cast Iron

Test Solution	Test condition at 50 C	Deepest metal penetration (mm)	Avg. metal penetration (mm)	Pitting factor*
Pure ethanol	Aerated	30×10^{-3}	21×10^{-3} 1.43	→
Pure ethanol+ 50%v/o water	Aerated	-	-	-
Pure ethanol	Non-aerated	-	-	-
Pure ethanol+ 50%v/o water	Non-aerated	-	-	-
Denatured ethanol	Aerated	3×10^{-3}	3×10^{-3}	1.00
Diluted denatured ethanol	Aerated	43×10^{-3}	18×10^{-3}	2.3
Denatured ethanol	Non-aerated	9×10^{-3}	3×10^{-3}	3.00
Diluted denatured ethanol	Non-aerated	63×10^{-3}	36×10^{-3}	1.7

$$\text{Pitting Factor} = \frac{\text{Deepest metal penetration}}{\text{Avg. metal penetration}}$$

Table 13: Pitting factor of gray cast iron in various test conditions.

MATERIAL : Gray Cast Iron

Test condition	No. of counts	No. of pits	Avg. No. of pits
Aerated pure ethanol at 50°C	1	11136	
	2	10428	10802
	3	10842	
Aerated denatured ethanol at 50°C	1	4632	
	2	4244	4406
	3	4342	
Aerated diluted denatured ethanol at 50°C	1	5864	
	2	5243	5524
	3	5464	
Non aerated denatured ethanol at 50°C	1	1898	
	2	1642	1779
	3	1796	
Non aerated diluted denatured ethanol at 50°C	1	2068	
	2	2482	2263
	3	2238	

Table 14: Pit density evaluation

SEALANT	STATE OF HARDNESS	LEAKAGE	SOLUTION COLOR CHANGE
Real Tuff	T	N	N
Harvey's Seal	T	N	N
Gripp	SH	Y	F
LA-CO Slick	T	Y	F
ZEP Pipe Seal	T	Y	N
Teflon Paste	T	N	N
Permatex	SH	N	N
Jomar-green stuff	H	N	N
Hercules Block	T	Y	F
HVAC Permatex	H	Y*	C
Pro-dope	H	N	N
LA-CO Anaerobic	T	N	N

State of hardness: T= Tacky, SH= Semi-hard, H= Hard.

Leakage: Y= Yes, N= No: Y*= Considerable leakage

Solution color: C= considerable, F= Faint, N= None.

Table 15: Summary of the sealant test results.

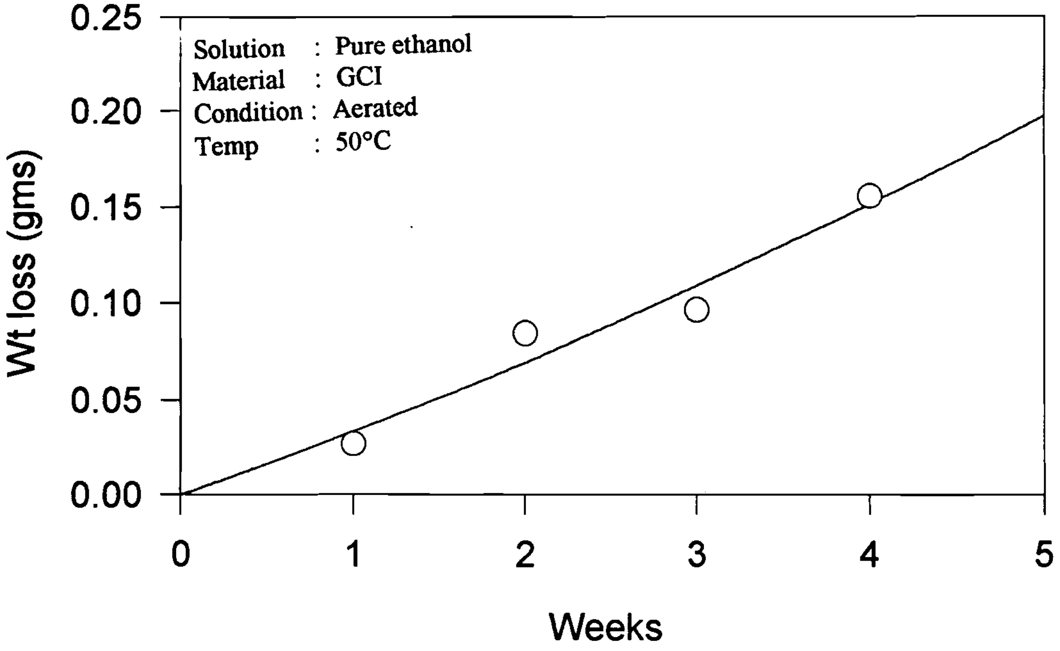

Fig 8: The plot shows corrosion rate to be minimal, but is linear, presumably, a protective film has not formed.

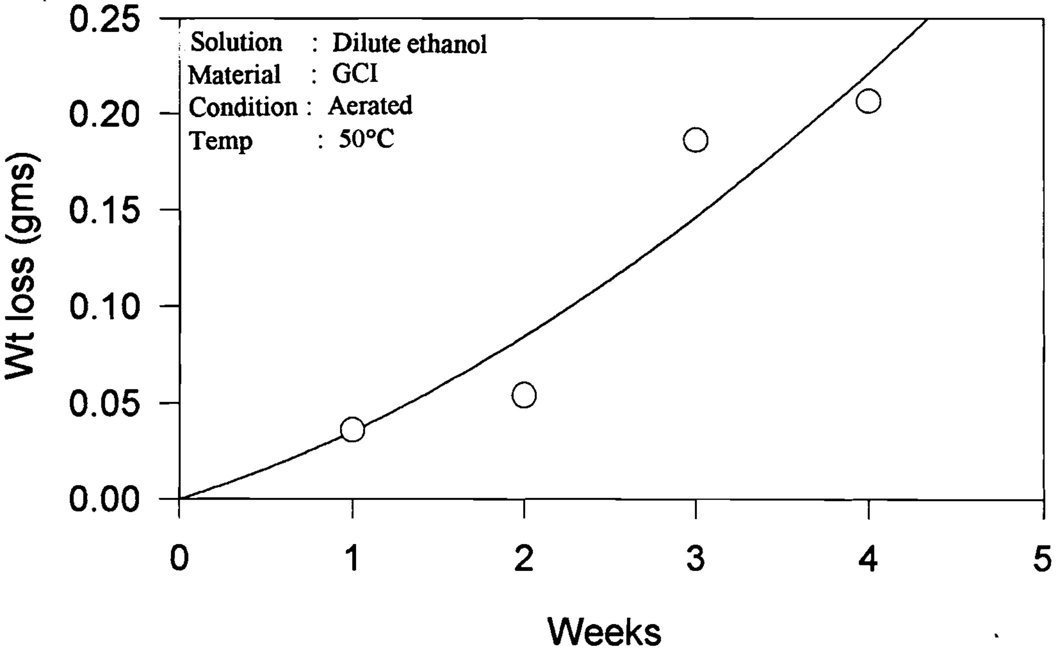

Fig 9: The plot shows the rate of weight loss to be maximum after the third week.

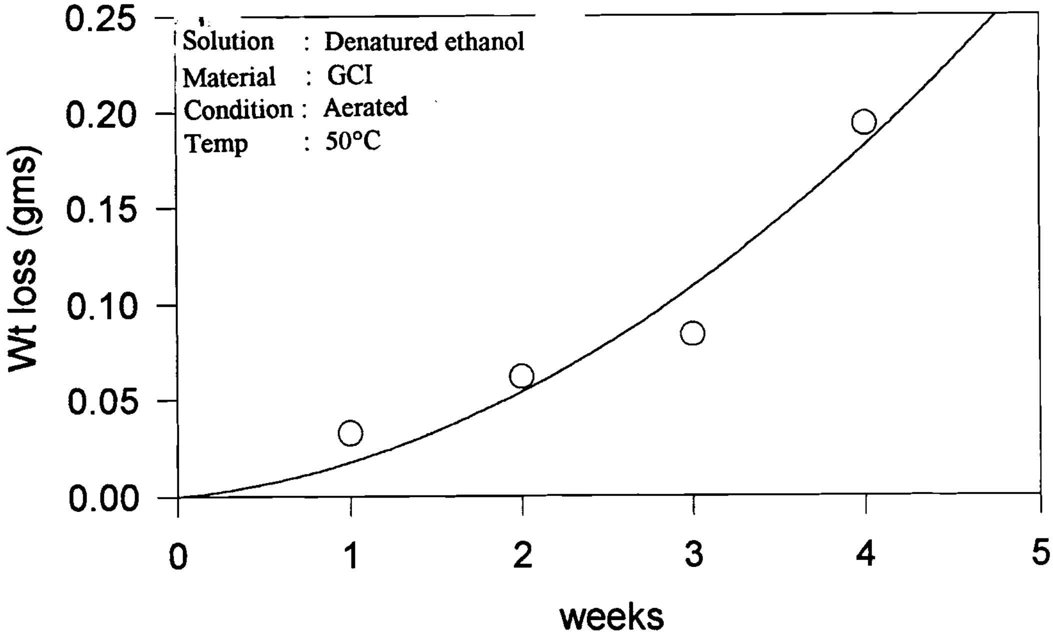

Fig 10: The corrosion rate is maximum in the fourth week. The corrosion rate at the end of four weeks is 1.7 MPY. This rate is low, although a protective film has not yet formed.

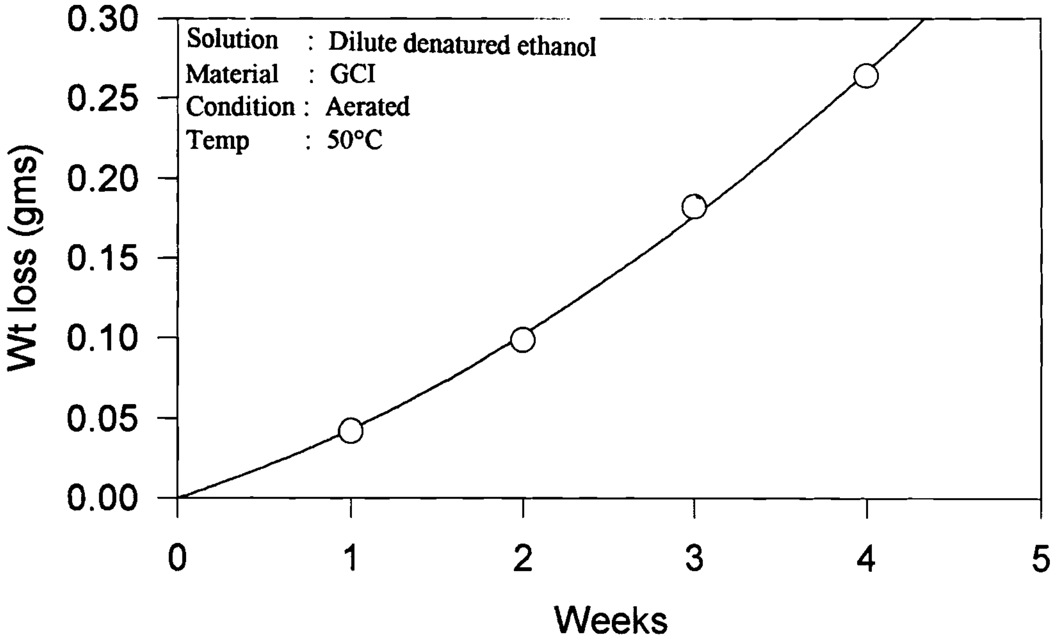

Fig 11: The plot shows a linear relation of weight loss with time. The corrosion rate at the end of fourth week is 2.3 MPY

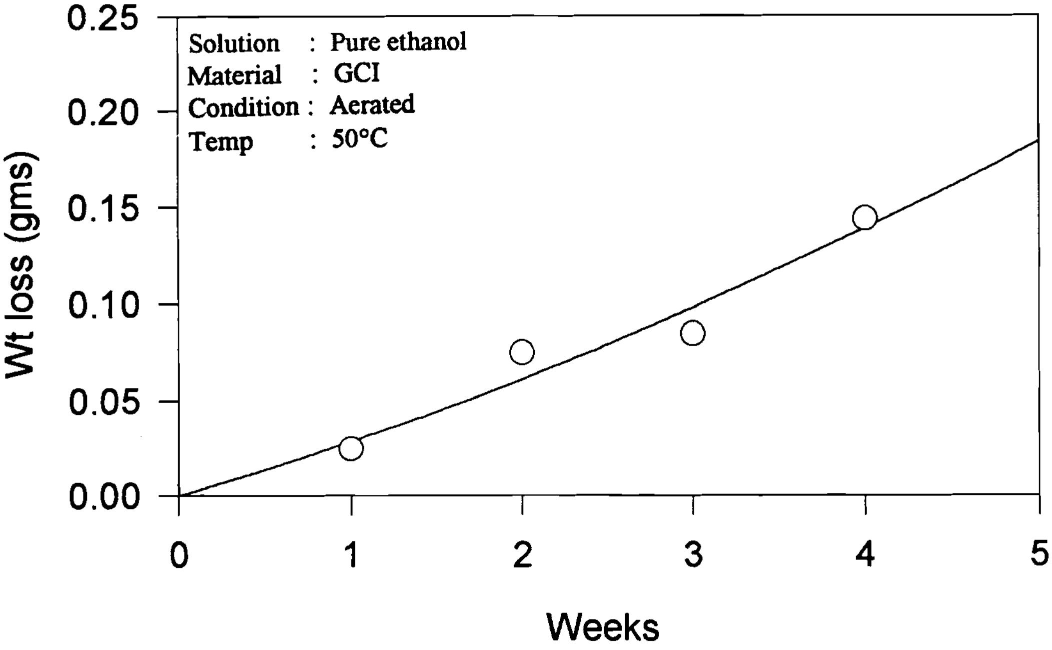

Fig 12: The weight loss has approximately a linear relation with time. The corrosion rate at the end of four week is 0.9 MPY

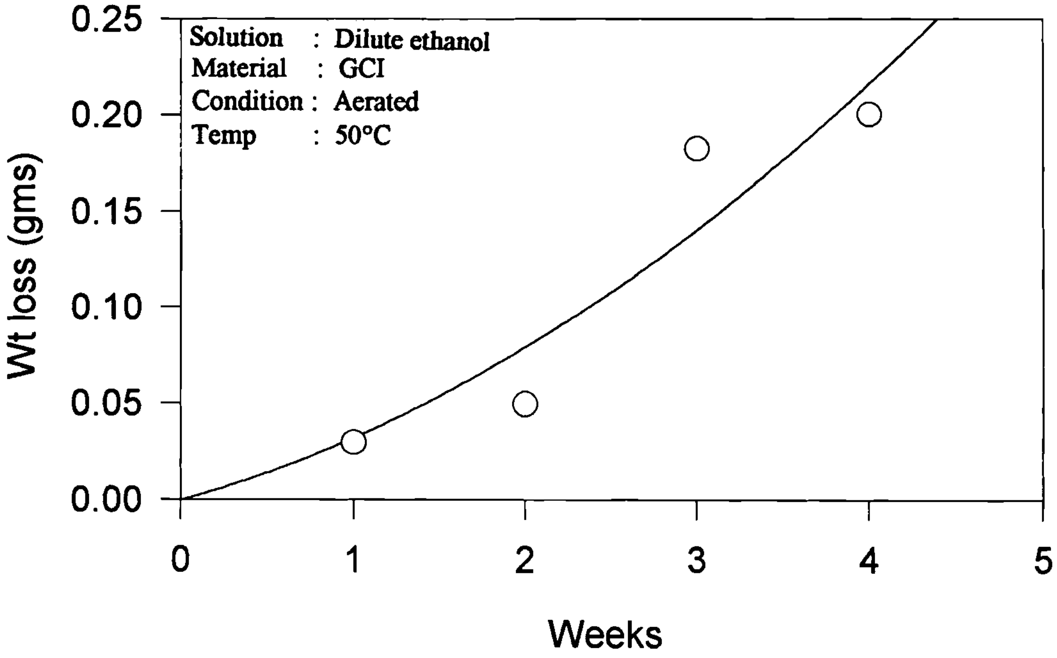

Fig 13: The corrosion rate is maximum in the third week as in the case of dilute pure ethanol.

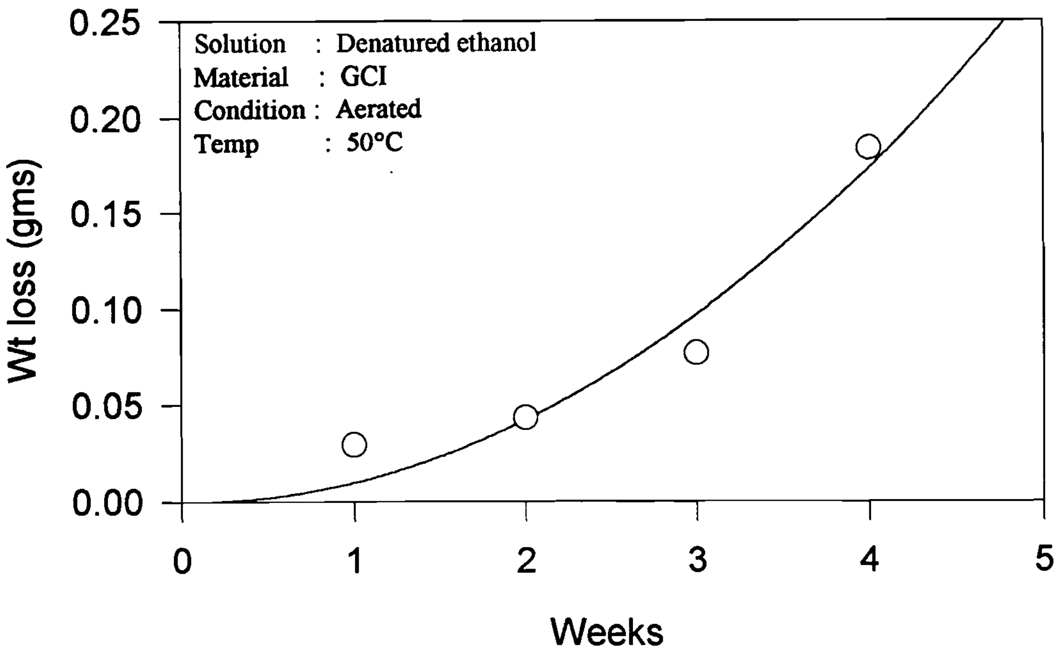

Fig 14: The corrosion rate is maximum in the fourth week as was the case in aerated denatured ethanol

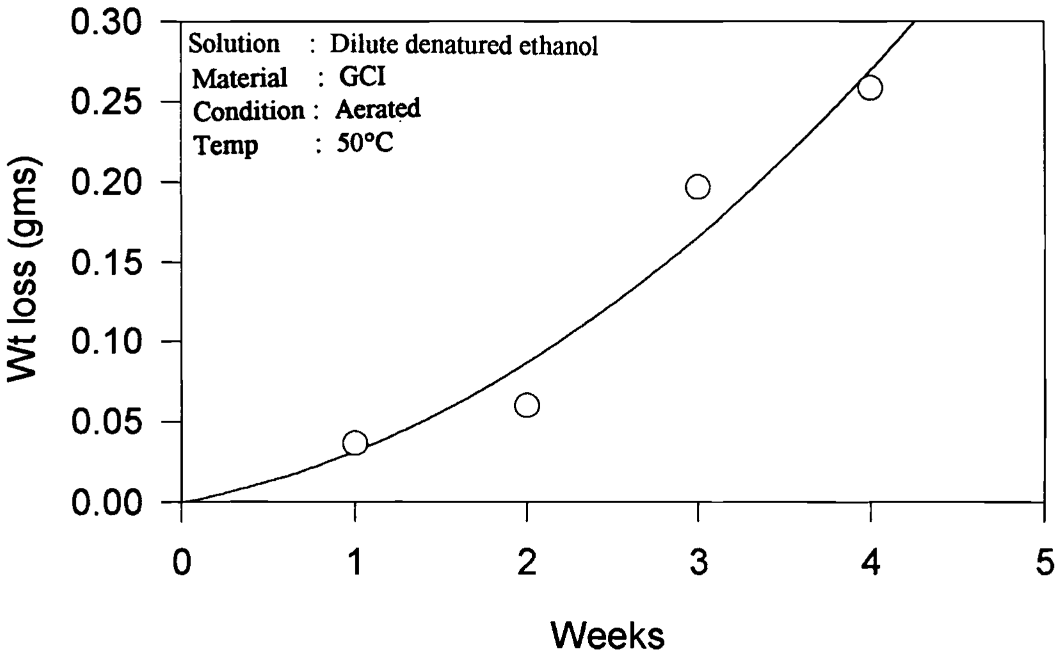

Fig 15: The corrosion rate is maximum in the third week with the rate being 1.1 MPY at the end of four weeks.

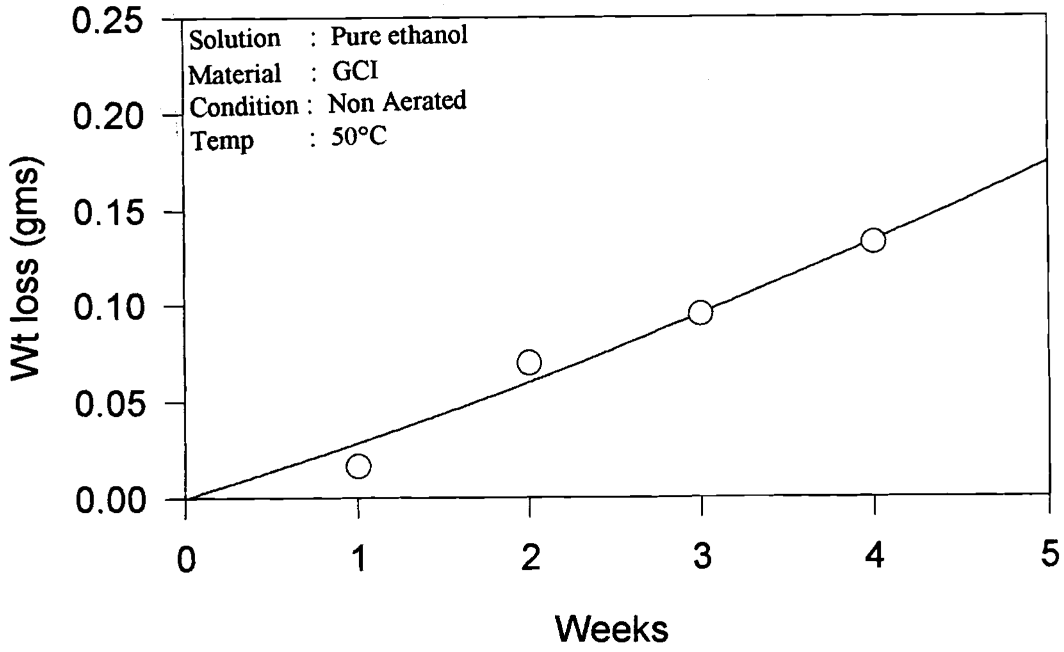

Fig 16: The weight loss is linear with respect to time, which could be due to the absence of a protective film.

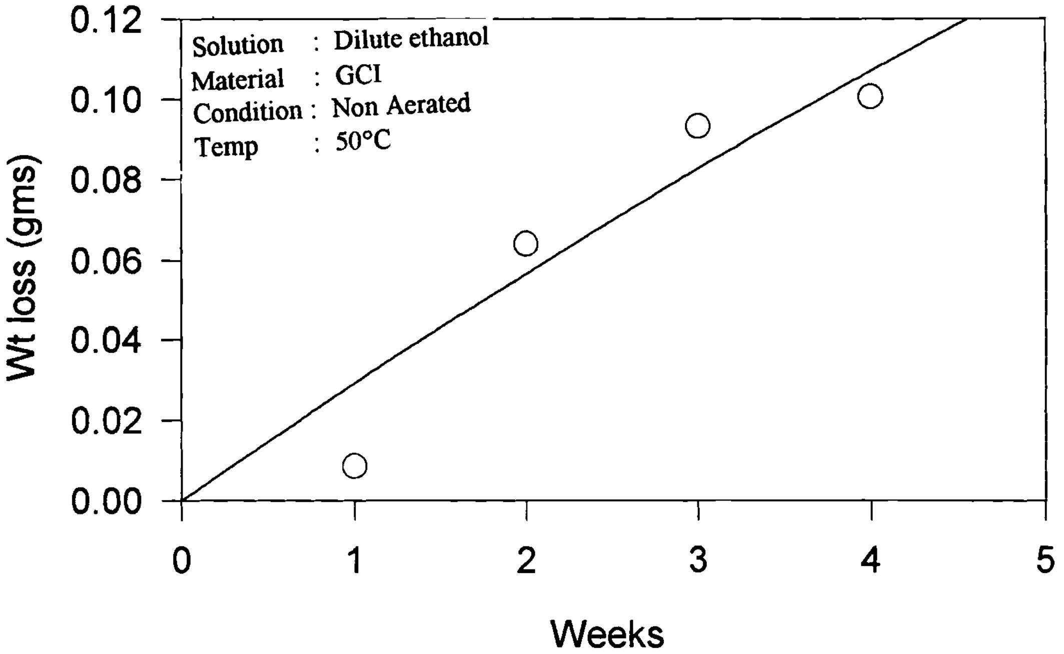

Fig 17: The corrosion rate is maximum in the second week and maybe approaching a pleteau after the fourth week.

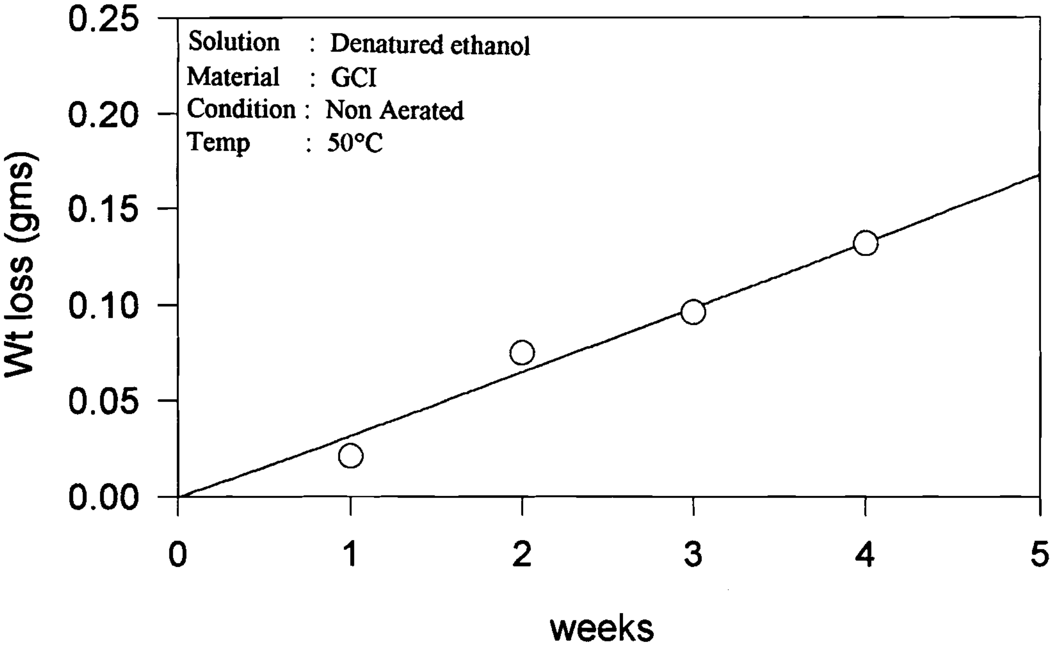

Fig 18: The corrosion rate is linear with respect to time. The corrosion rate is 1.6 MPY at the end of four weeks.

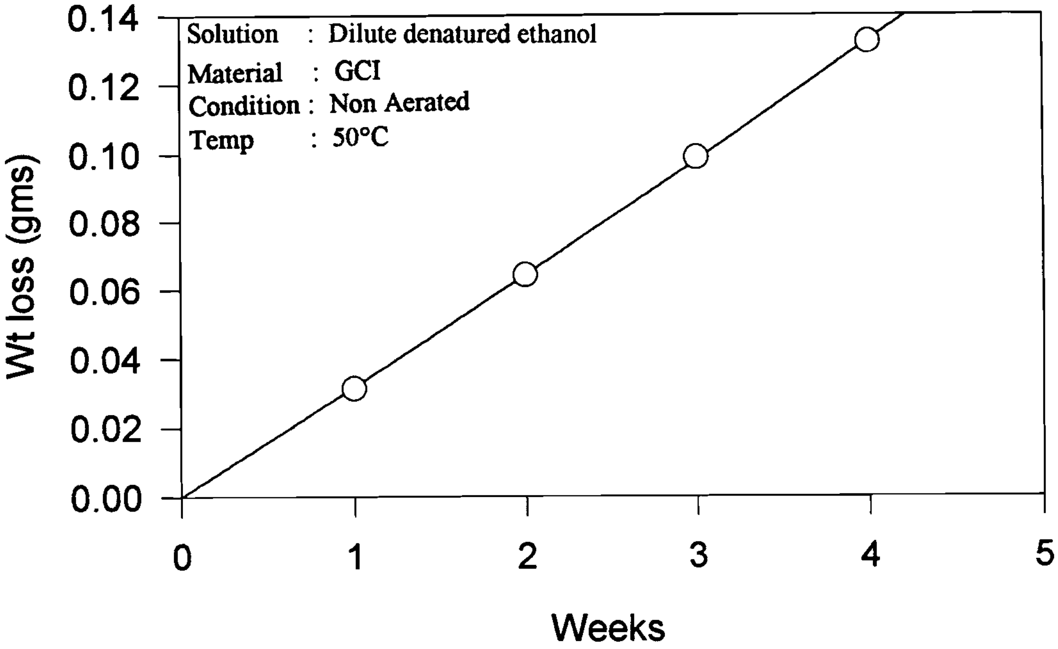

Fig 19: The corrosion rate at the end of 4 weeks is 2.2 MPY

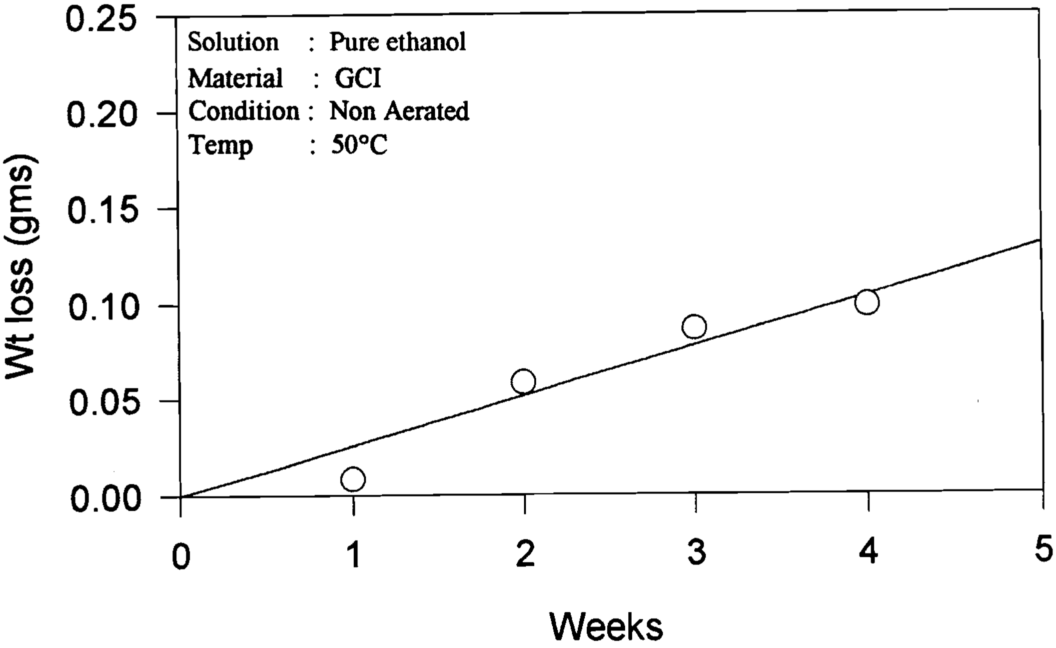

Fig 20: The weight loss seems to be achieving a plateau in the fourth week.

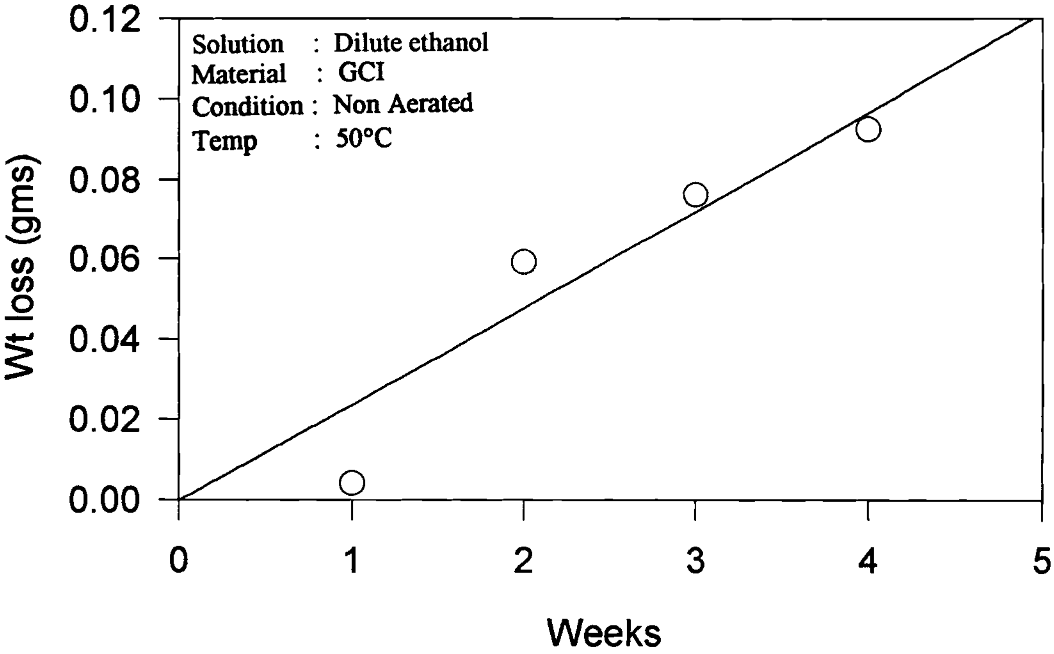

Fig 21: The maximum weight loss occurs in the first week. The reduction of corrosion rate in the latter weeks could be to the formation of a protective film.

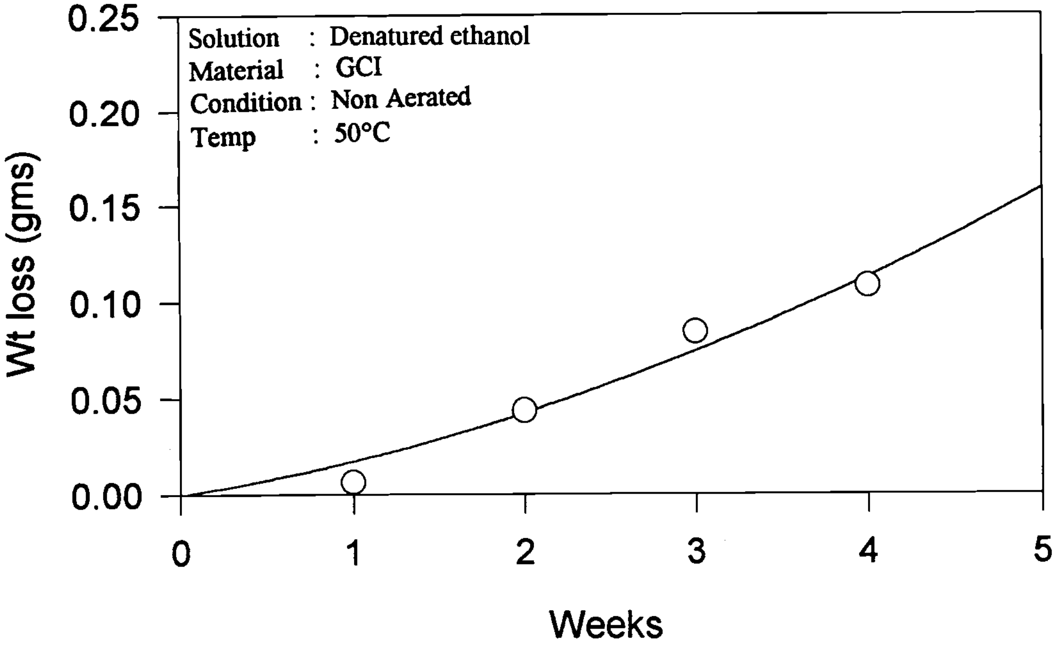

Fig 22: The corrosion rate at the end of four weeks is 0.93

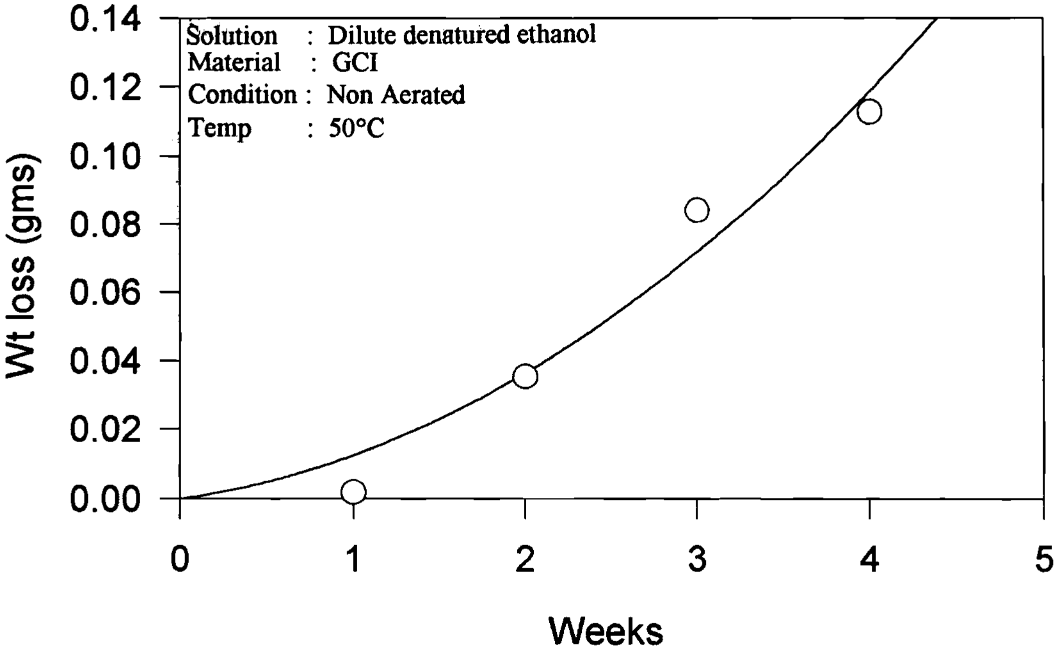

Fig 23: The weight loss is maximum in the third week, but starts reducing in the fourth week, may be on account of film formation.

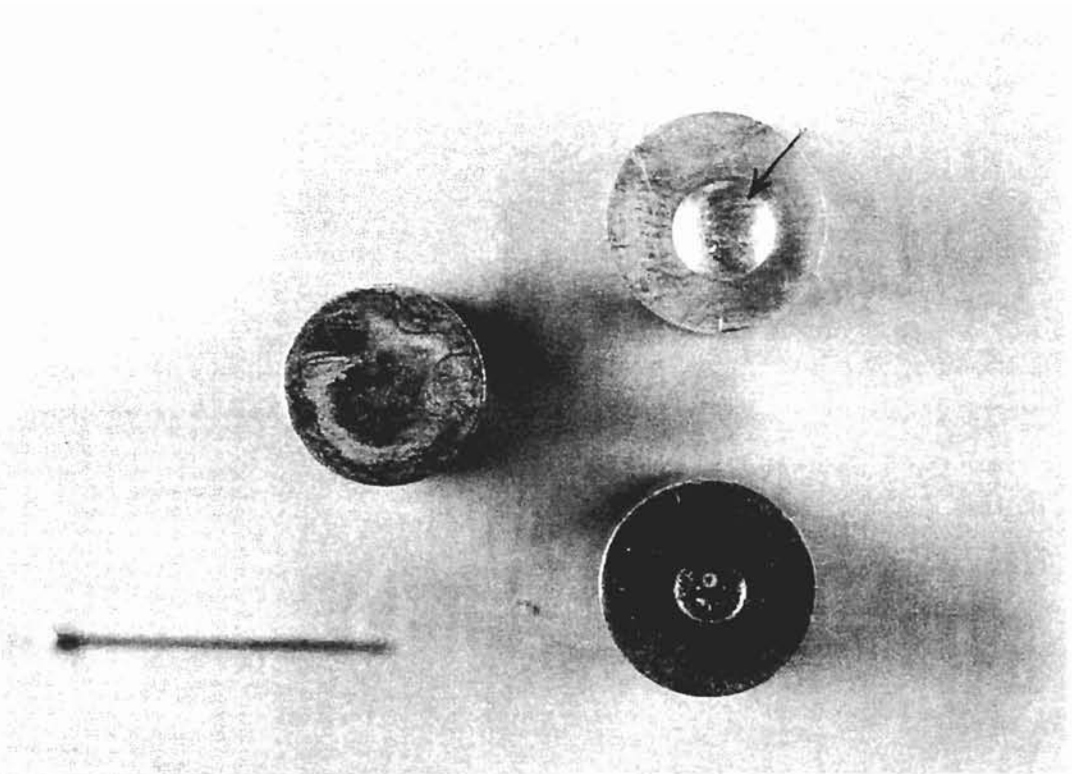

Fig 24: Cylindrical immersion test specimens of Brass, stainless steel and Gray cast iron. Arrow indicates the indent to induce residual stress and possible SCC.

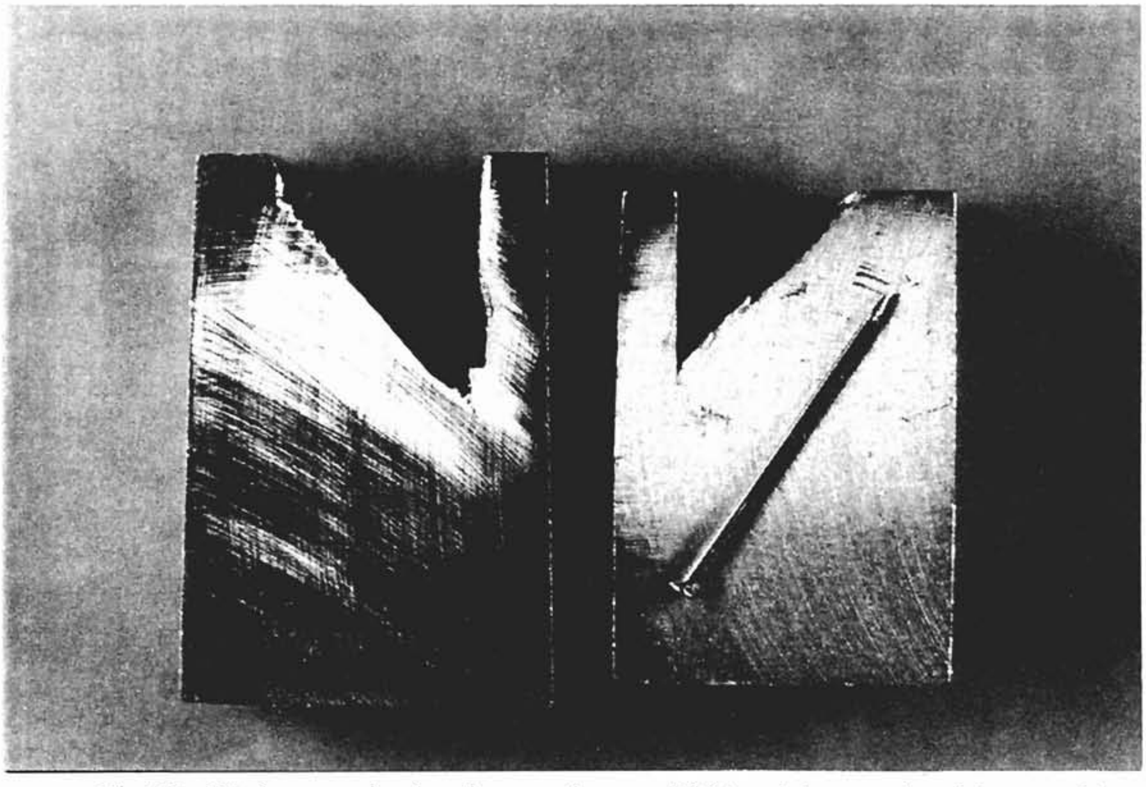

Fig 25: Wedge opening loading specimens of 304 stainless steel and brass with a rough machined V-notch of 40°± 2°

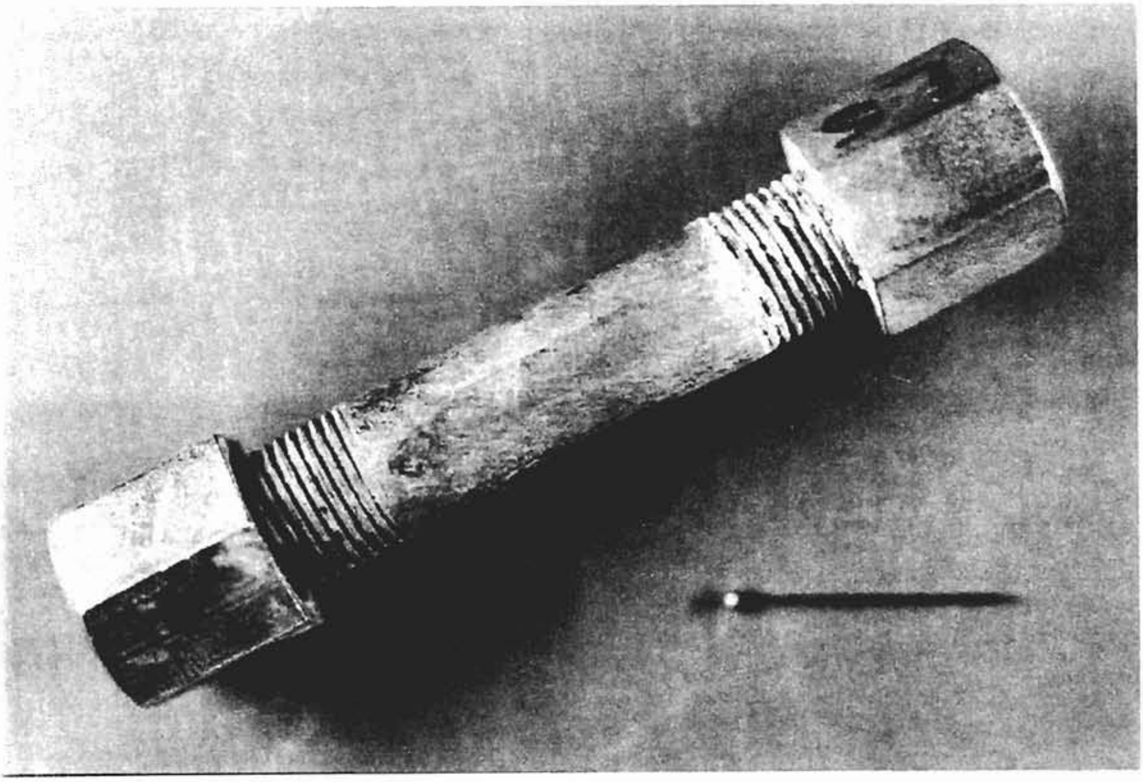

Fig 26 : Sealant specimen showing smears on the surface indicating leakage after 6 weeks of immersion in absolute ethanol

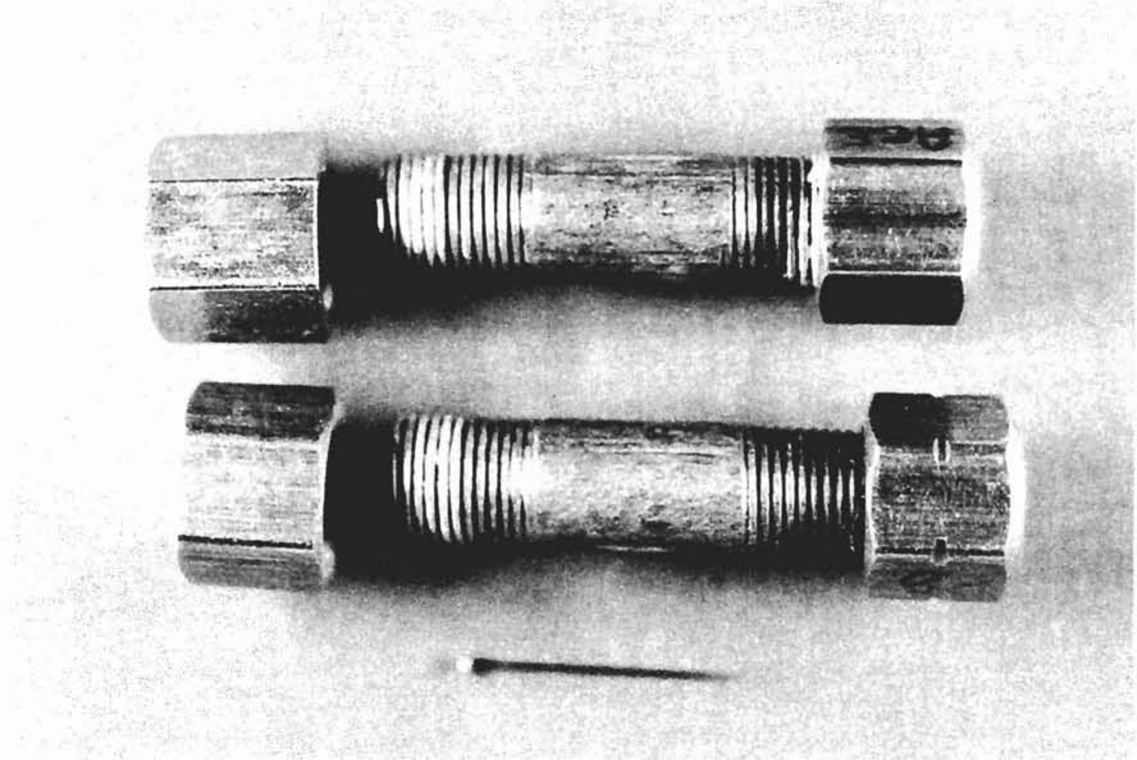

Fig 27 : Sealant specimens after 6 weeks immersion in absolute ethanol showing no leakage

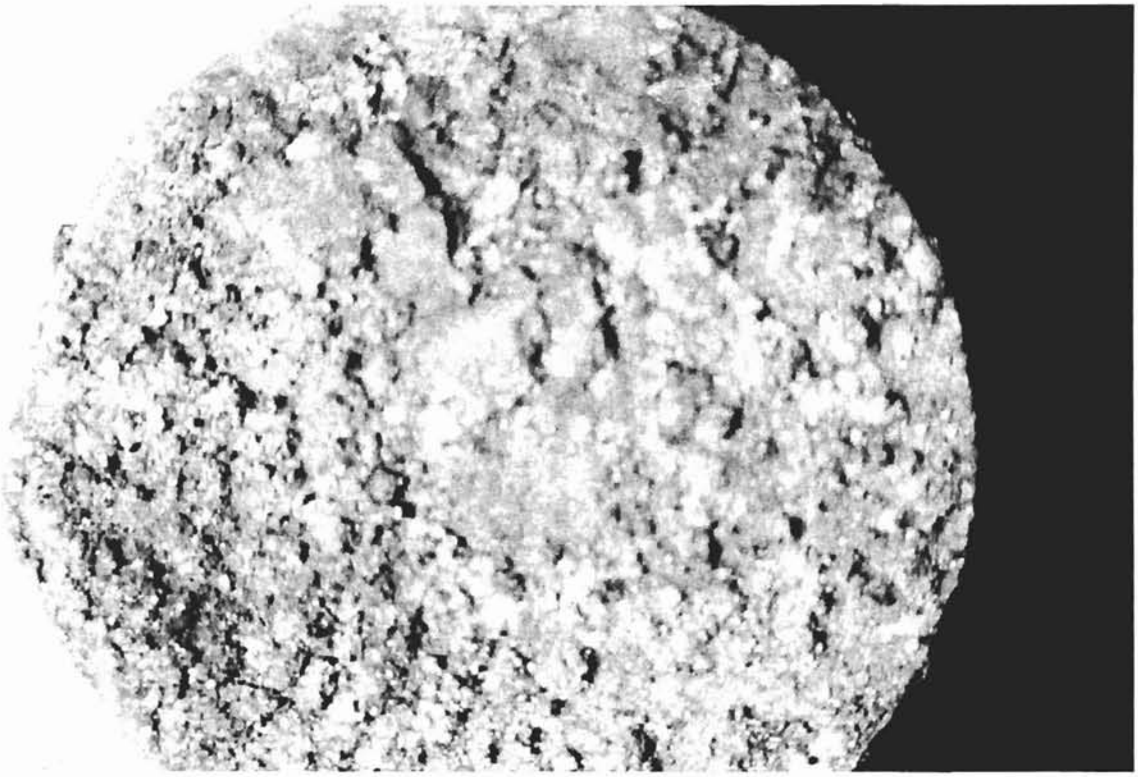

Fig 28: Top surface of Gray Cast Iron specimen showing muddy brown deposit after 4 weeks of immersion in aerated dilute denatured ethanol

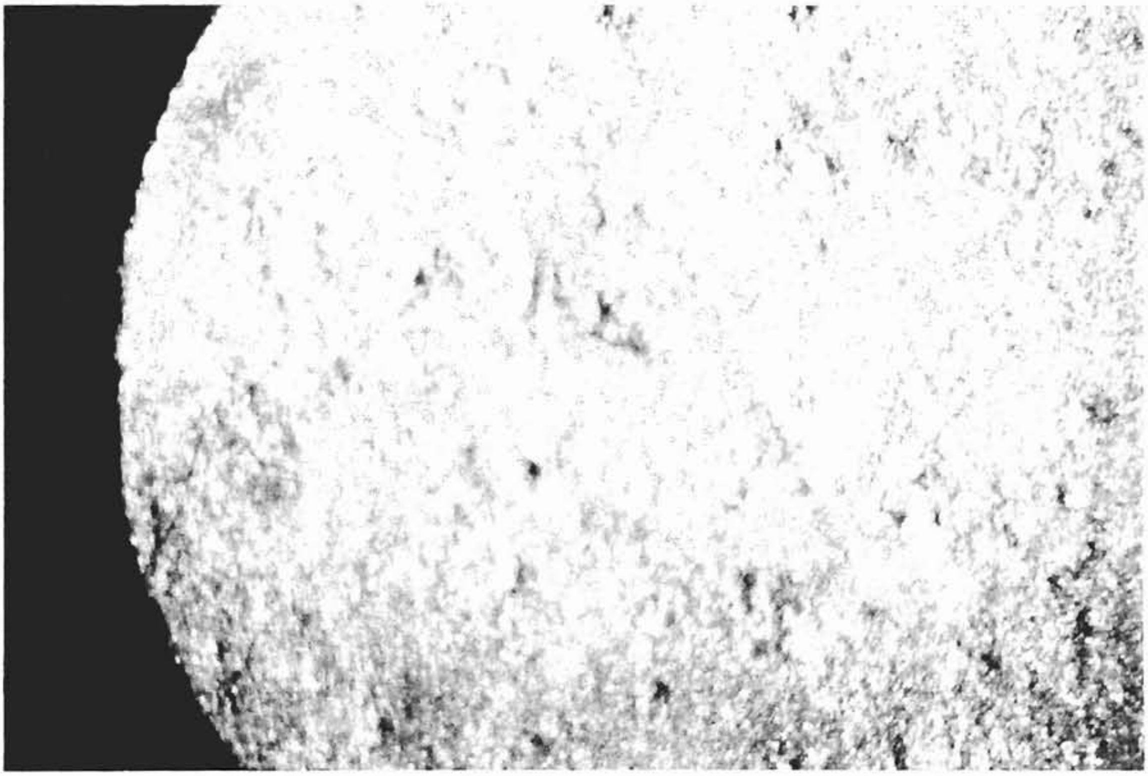

Fig 29: Top surface of specimen in Fig 28, after chemical cleaning showing uniform pitting all over the surface

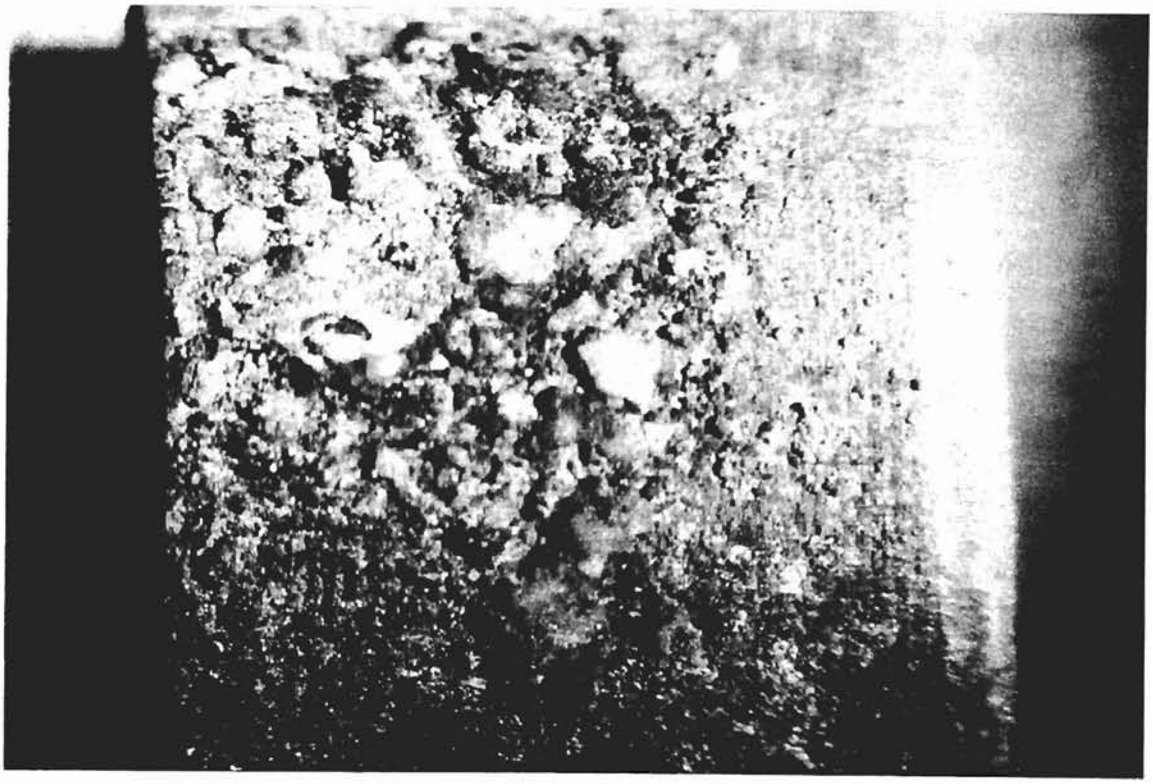

Fig 30: Side view of Gray Cast Iron specimen after immersion for 4 weeks in aerated dilute denatured ethanol. The attack and deposition decreased progressively towards the bottom surface.

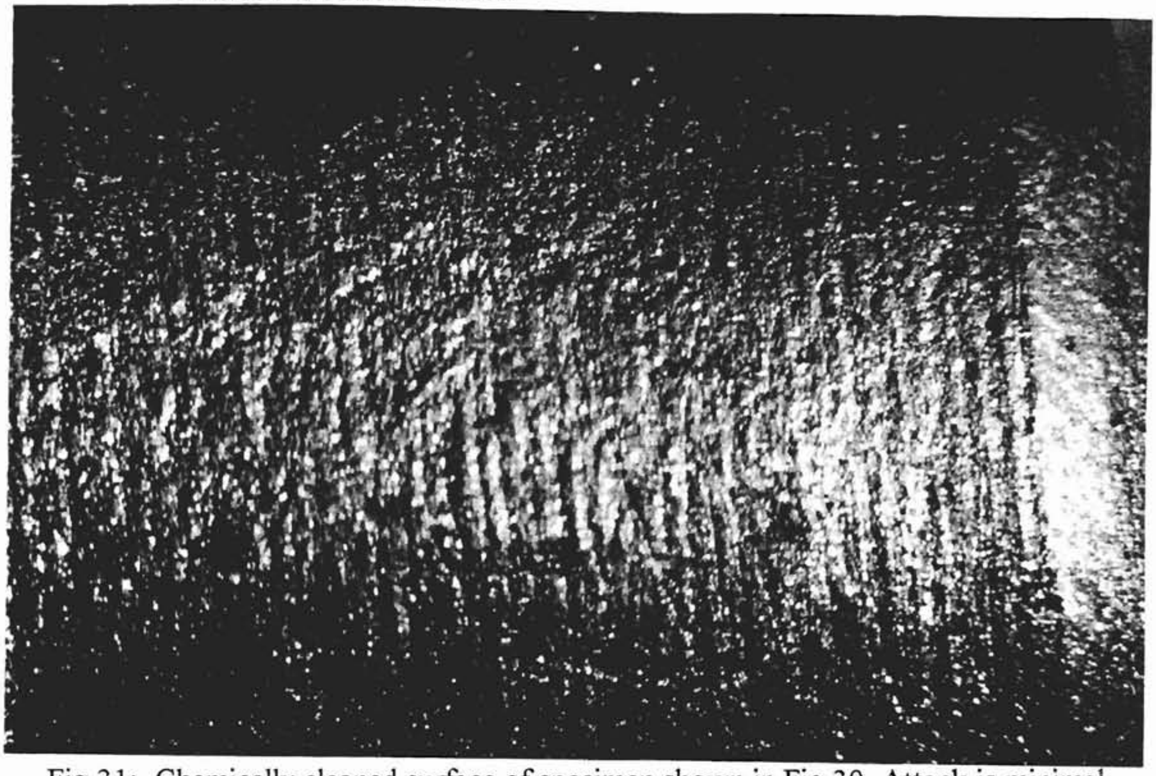

Fig 31: Chemically cleaned surface of specimen shown in Fig 30. Attack is minimal

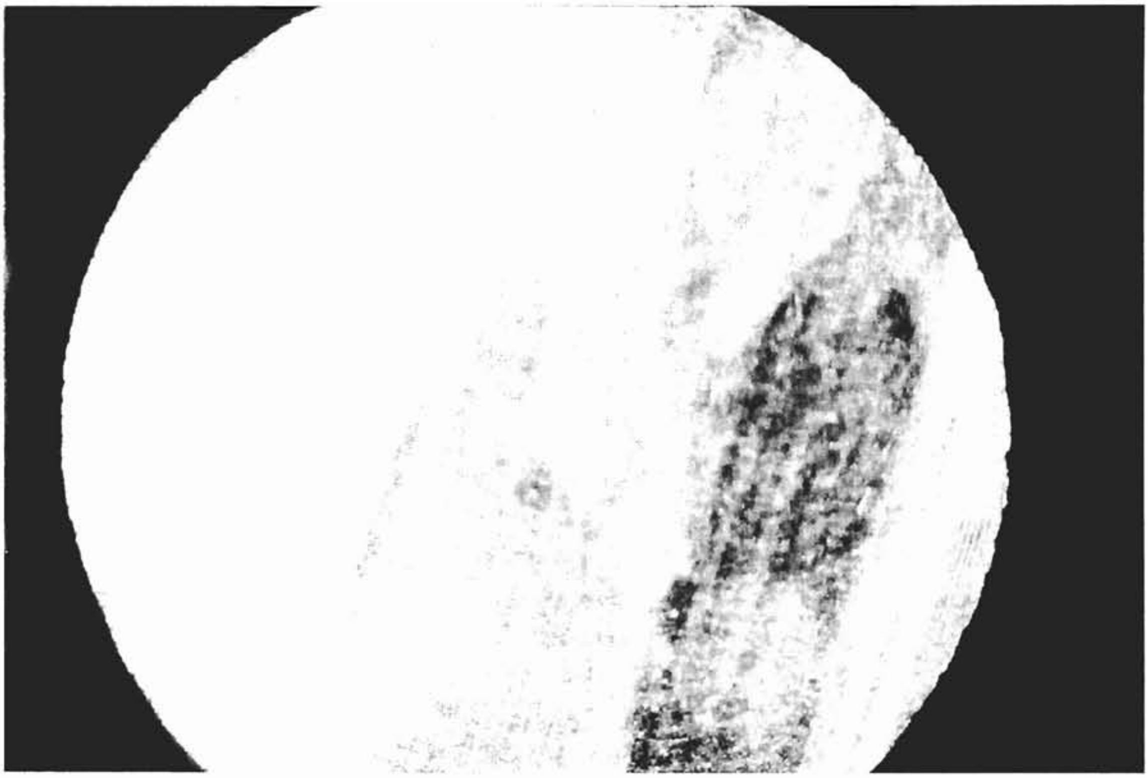

Fig 32: Gray Cast Iron specimen after immersion in aerated dilute absolute ethanol for a period of 4 weeks. The bright surface indicates that attack is minimal.

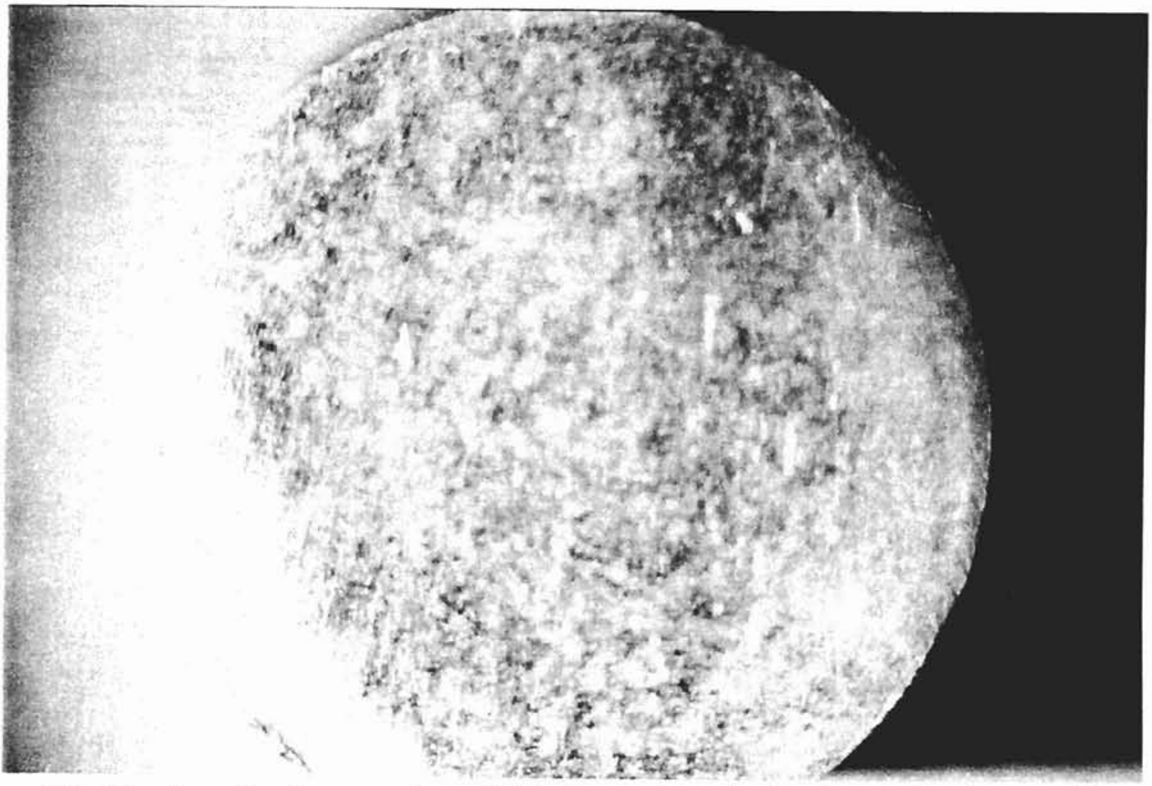

Fig 33: Gray Cast Iron specimen finished over 240 grit after immersion in aerated dilute absolute ethanol for a period of 4 weeks. It shows minimal attack.

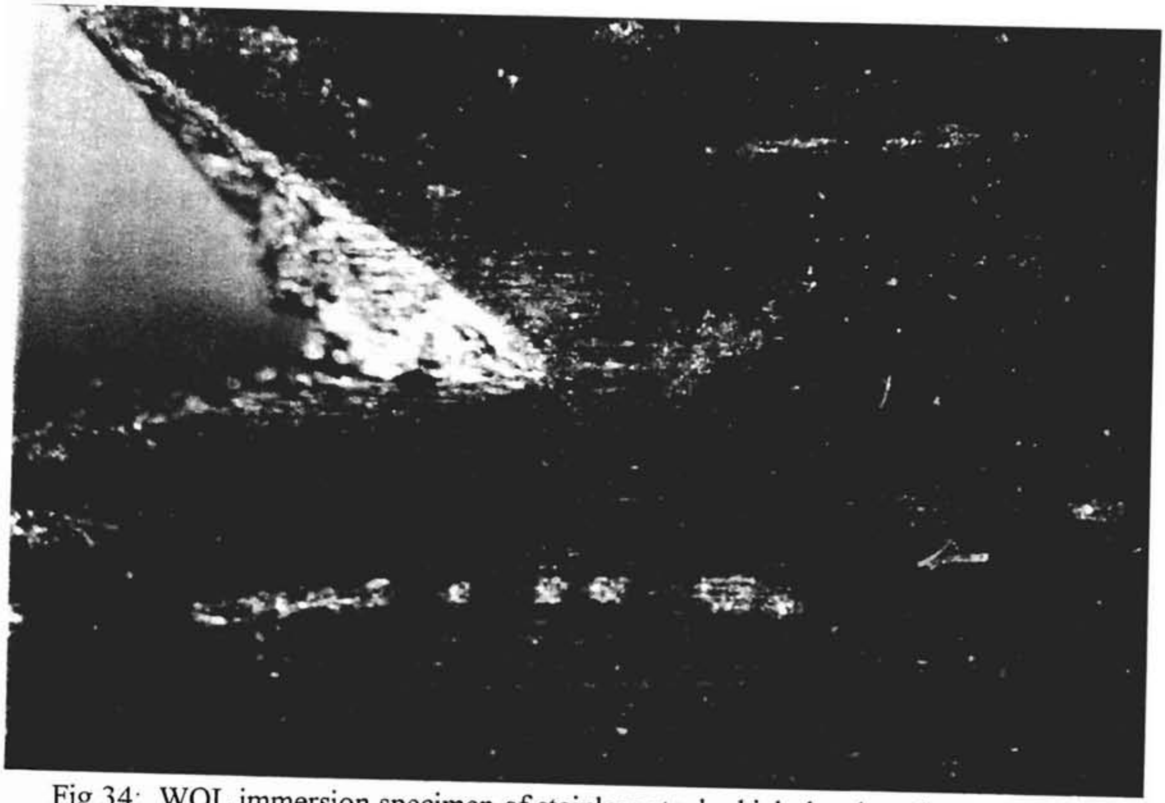

Fig 34: WOL immersion specimen of stainless steel which developed a crack at notch root after 4 weeks of immersion in pure denatured ethanol(aerated)

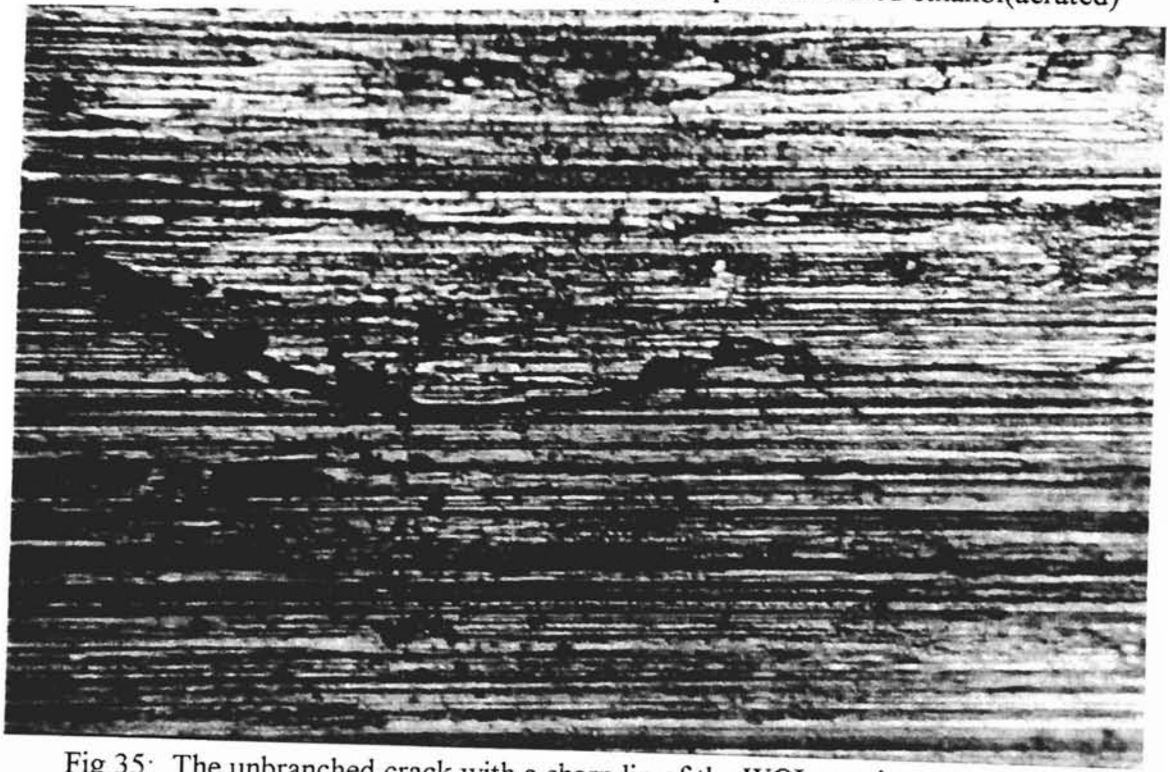

Fig 35: The unbranched crack with a sharp lip of the WOL specimen of stainless steel shown in fig 34.

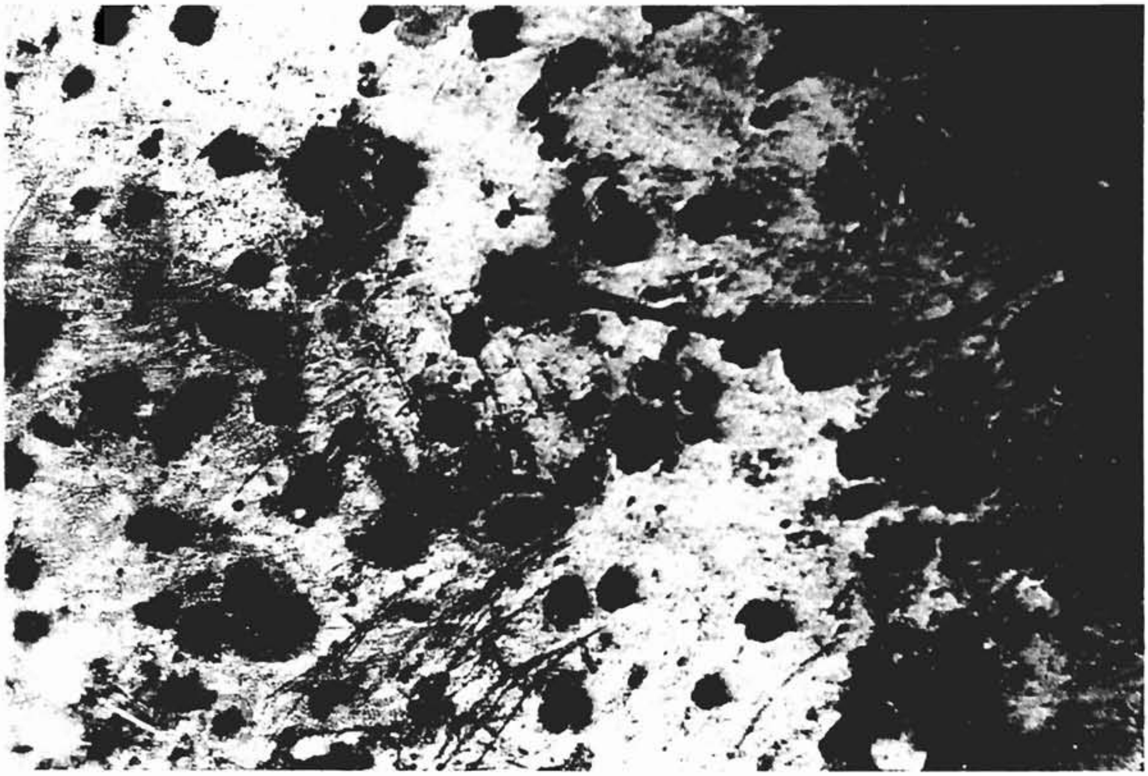

Fig 36 : Pitting corrosion of Gray Cast Iron in aerated pure ethanol solution after 4 weeks of immersion (240 grit finish).

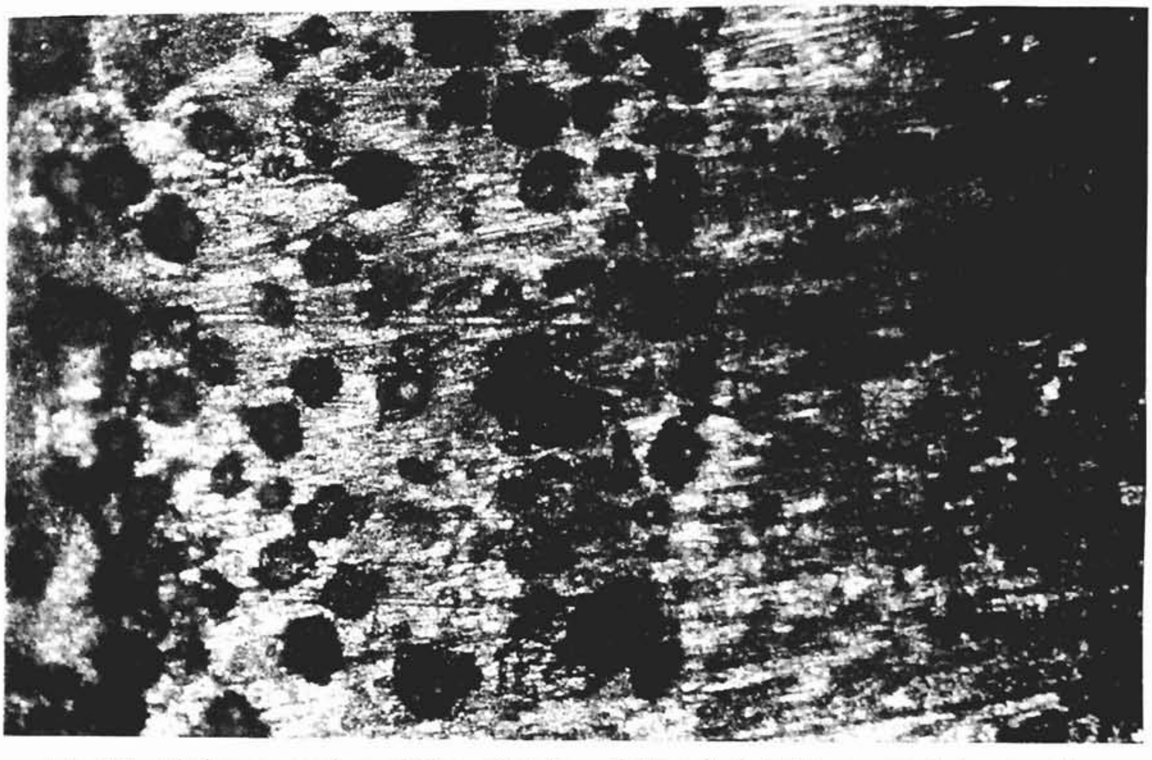

Fig 37: Pitting corrosion of Gray Cast Iron (600 grit finish) in aerated denatured ethanol after 4 weeks of immersion

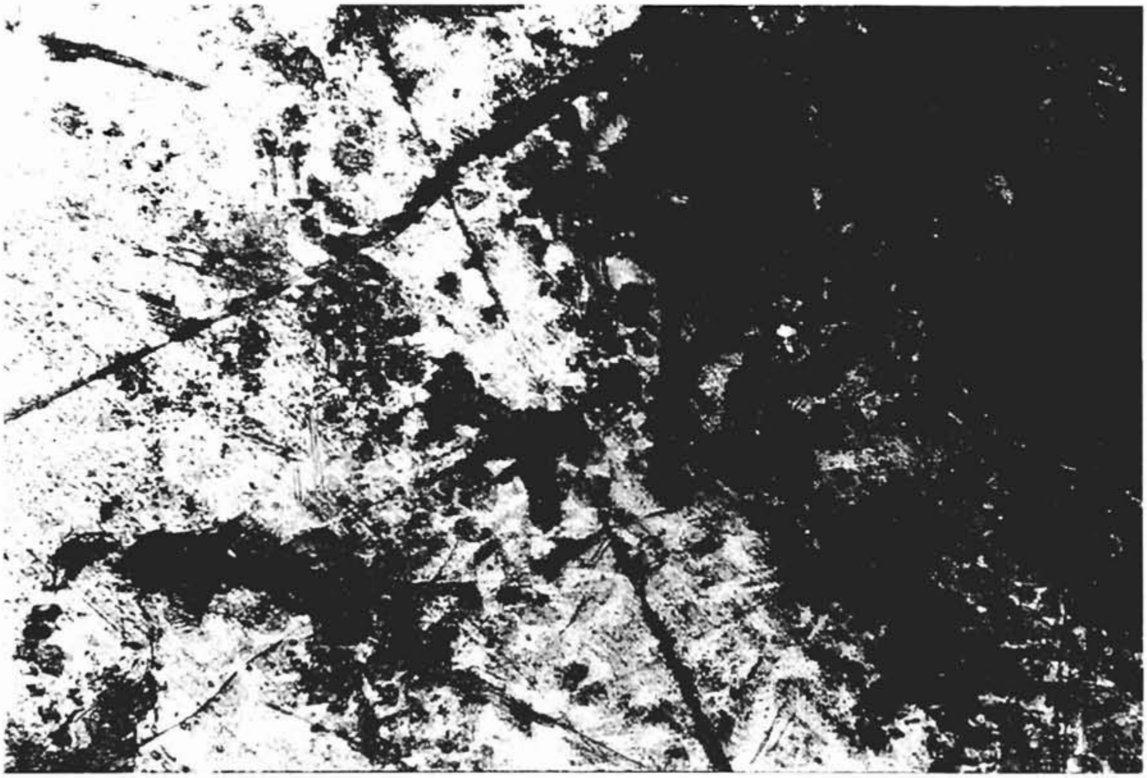

Fig 38: Crevice corrosion of brass specimen. The dark region is the zone of attack. The specimen was immersed in denatured ethanol for 4 weeks.

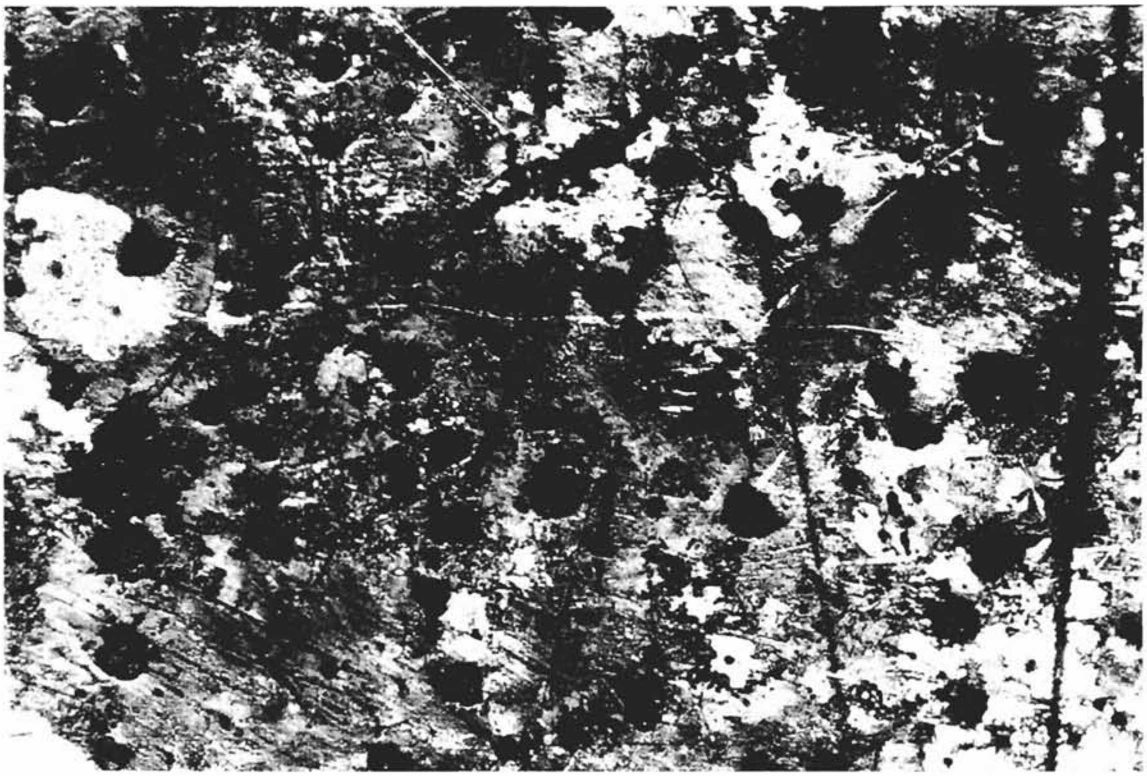

Fig 39: Pitting Corrosion of the brass specimen after immersion in denatured ethanol for 4 weeks

Fig 40: Immersion test beakers maintained at test temperature in fume hood

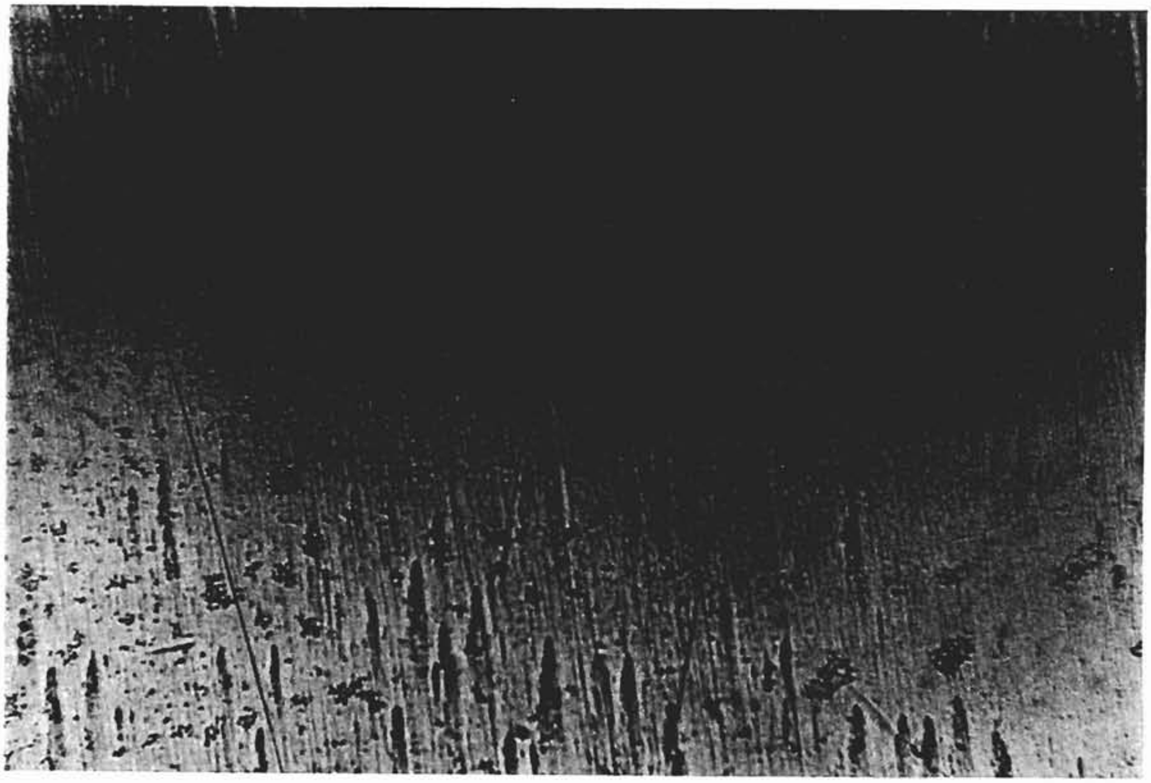

Fig 41: Unaffected surface of stainless steel in environol (325X)

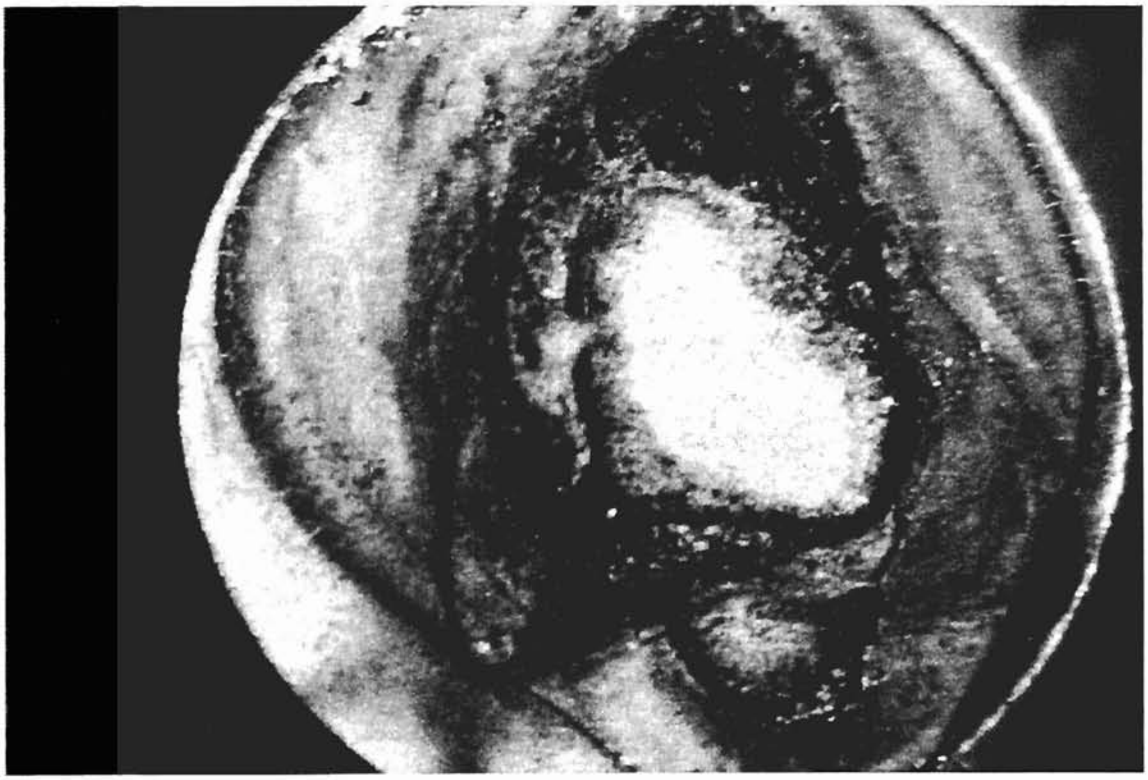

Fig 42: Cylindrical specimen of GCI showing crevice corrosion after immersion in environol for 4 weeks.

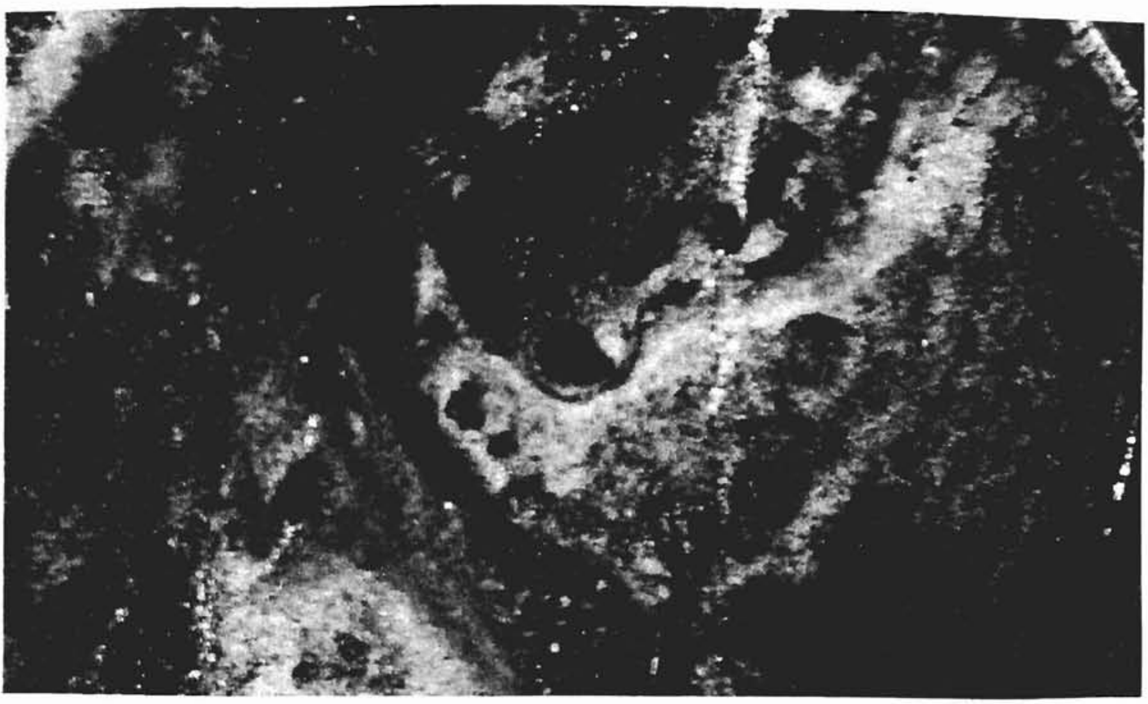

Fig 43: Crevice corrosion of gray cast iron specimen shown in above fig at a higher magnification (325X)

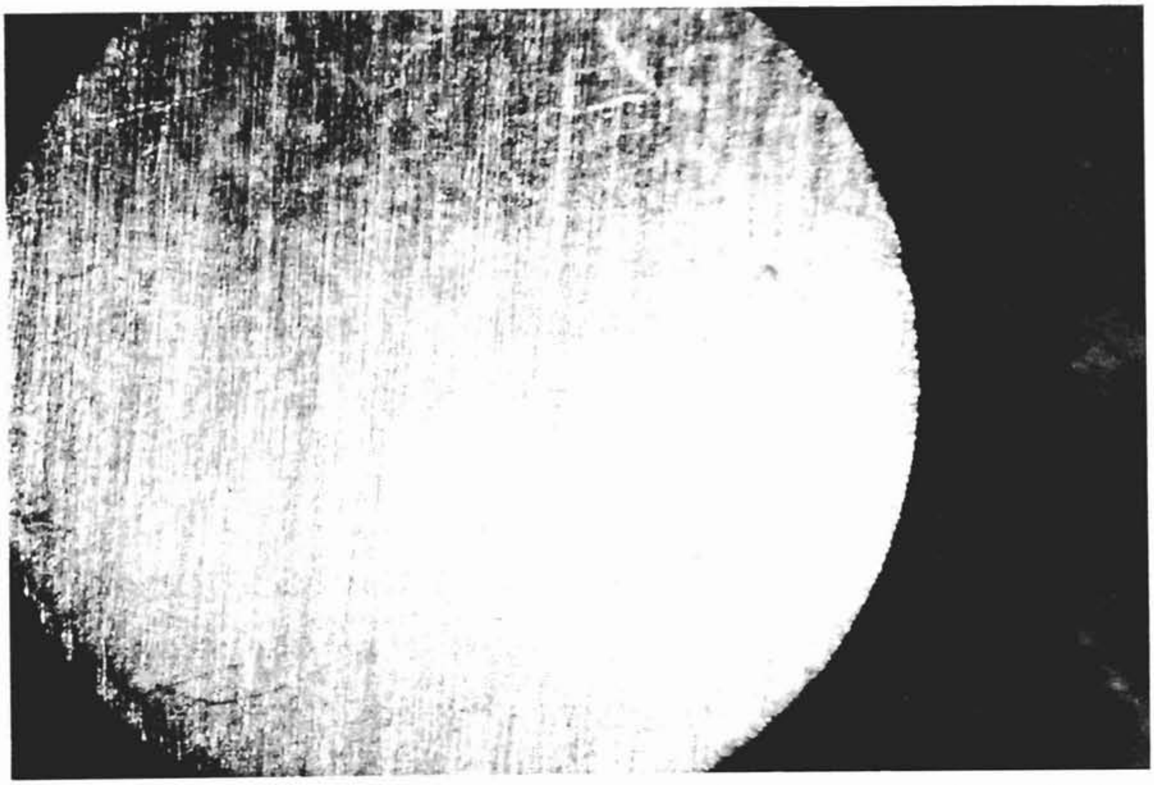

Fig 44: The top surface of brass specimen showing no attack after immersion in environol for 4 weeks (13X)

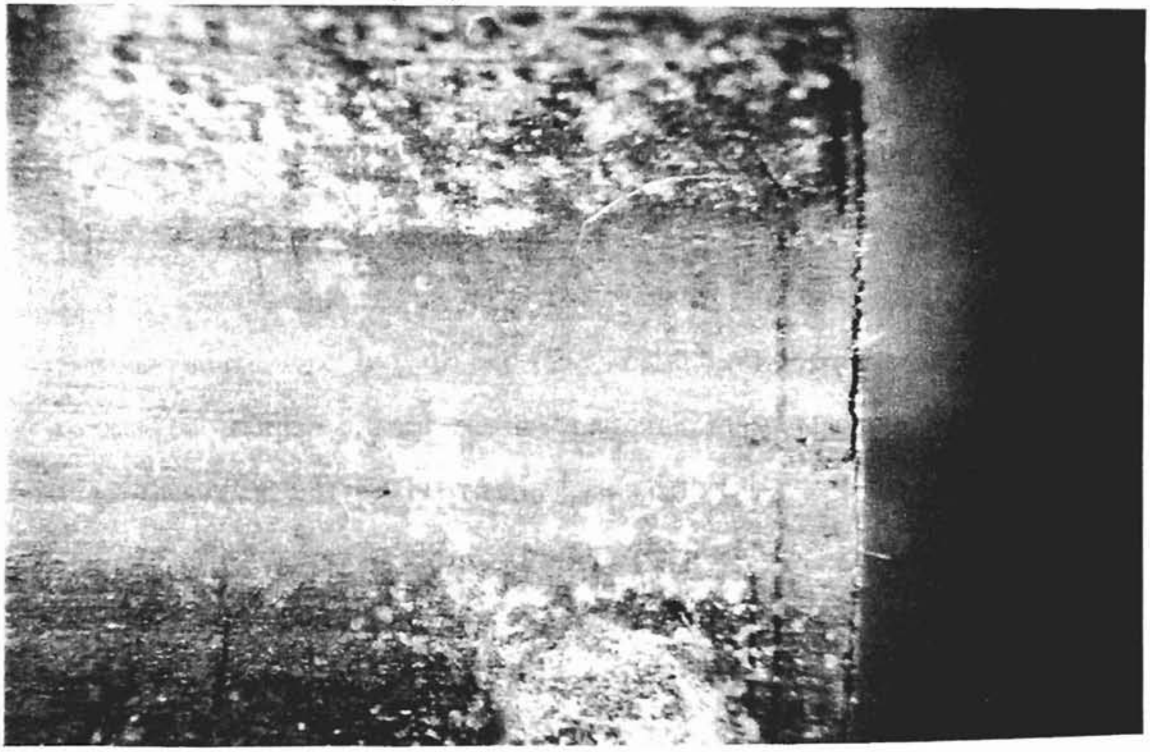

Fig 45: Side view of the brass specimen showing white deposition after immersion in environol for 4 weeks.

CHAPTER V

DISCUSSION

1.METALS

As was apparent from the review of literature, any corrosivity with alcohols is due to the acid residues left behind in the manufacturing process, oxygen, any electrolytes and the water used for dilution. Ethanol itself is a poor electrolyte with a specific conductivity of 1.35×10^{-9} mhos compared to 5×10^{-7}mhos of water.

In accord with the foregoing, the attack in absolute ethanol was minimal. The solubility of oxygen is 25 vol per 100 vol of alcohol compared to 88.88% in water. Moisture and oxygen can be picked up while pouring, though extreme care was taken to minimize exposure. The traces of deposition and attack on GCI must be due to the acid residues (common in alcohols), moisture and /or oxygen.

The behavior of metals in denatured ethanols is effected by the denaturants (electrolytes) and the water composition. The reddish brown deposites of oxides of iron and traces of pitting are a consequence of the electrochemical reactions. Chemical grade denatured ethanol contains methanol, as a denaturant,that increases the corrosivity of the solution. The shorter chain aliphatic chain length of methanol seems to afford lesser corrosion protection on account of higher conductivity than ethanol. In commercial denatured ethanol, brass and stainless steel remained relatively unaffected as in absolute alcohol and denatured ethanol. Sodium meta bisulfite present in "Environol" is an oxygen purger, which explains the reduced attack on cast iron.

With the introduction of water, the solution becomes conducive to electrolytic corrosion. The characteristic electrochemical reactions of electrolytic corrosion could be represented as follows. At the anode, in general, oxidation of the metal to its ions takes place by the reaction

$$M \text{ -----> } M^{n+} + ne^-$$

and for iron in specific,

$$Fe \text{ -----> } Fe^+ + 2e^-$$

At the cathode, it is the reduction of dissolved oxygen that is often observed in neutral and acidic solution exposed to ambient air. The reduction proceeds primarily according to the reactions

$$O_2 + 2H_2O + 4e^- \text{ ------> } 4\ OH^- \text{ (in alkaline or neutral solutions)}$$

$$O_2 + 4H^- + 4e^- \text{ ------> } 2H_2O \text{ (in acidic solutions)}$$

In the absence of the above two reactions, water will be reduced by a reaction which is equivalent to the dissociation of water and is given by

$$2H_2O + 2e^- \text{ ---------> } H_2 + 2OH^-$$

In denatured ethanol, the presence of denaturants and water make the solution an electrolyte. The presence of water increases the oxygen solubility, which enhances the reduction reaction and thereby corrosion. The cylindrical specimens of stainless steel and brass remained unaffected. However, the WOL specimen of stainless steel developed an unbranched crack with a sharp lip at the notch root which is characteristic of SCC. In a study by Farina et al., (24), it was found that low alloy steel specimens developed cracks in ethanolic and methanolic environments in the presence of an electrolyte. The presence of denaturants, methanol and water(5%) must have made the solution conducive to SCC. The crack which developed on the ninth day of immersion did not show any subsequent growth which could be on account of the reducing stress at notch root due to crack opening. It is to be noted that this WOL study was purely qualitative as fatigue precracking was not used. Crack growth sessetion correspond to a SCC threshold stress. It has been found that the presence of water even at low concentrations (<5%), leads to the formation of a passive protection film, which is essential for SCC. The 304 stainless steels depend on oxygen for the formation of passive film in active environments. At higher temperatures, it is the formation of a true oxide which prevents corrosion. A hydrated chromium oxyhydroxide film is formed in organic media and the dissolution and passivation mechanism remains the same in solutions containing 5 to 100 vol% water (25).

1.1 Effect of Aeration

Aeration of the solution increased the corrosion rate. As already explained, the higher oxygen content facilitates the corrosion enhancing reduction reaction.

The higher rates of corrosion in non aerated solutions could be explained by the failure of oxygen to escape at the testing temperature, increasing corrosion rates linearly with time. The increase in corrosion in the later weeks of testing, was because of the addition of solution/water, to maintain the concentration of the solution which provided more dissolved oxygen for corrosion to proceed, after the expenditure of all dissolved oxygen in the solution. In the case of GCI pitting was more severe in non aerated, dilute solutions than in aerated solution. In the presence of very little dissolved oxygen, a magnetite film is formed that is adherent to the surface. However, the pits already formed will act as anodes due to the depression of the pH at the pit bottom compared to the surface and thereby cause further pitting. The crevice corrosion observed in commercial denatured ethanol could be due to the differences in oxygen concentration between the shielded environment of the crevices and the surrounding area. The outer area, being higher in oxygen, is predominantly cathodic. Anodic dissolution occurs in the area where the solution remains stagnant and is lower in oxygen.

1.2 Effect of Dilution

The corrosion rates increased with dilution. With dilution, the solution becomes conducive to electrolytic corrosion. The higher content of water increases the concentration of dissolved oxygen, as well as the ability of the solution to retain oxygen, which facilitates reduction reaction enhancing reaction. The decreasing rate of corrosion, even in dilute solutions with increasing time is due to the formation of an oxide as a protective film on the surface. The oxides of iron Fe_2O_3 and Fe_3O_4 are stable over a wide range of pH and potential (10). A passive film is formed by the direct electrochemical reaction

$$Fe + 2H_2O \text{ --------> } Fe(OH)_2 + 2H^+ + 2e^-$$

In the case of stainless steel, as already mentioned, the dissolved oxygen helps in the formation of a passive film which is evident from the loss of brightness. The active to passive transition in 304 stainless steel depends on water content. However, once the hydrated chromium oxy hydroxide film is formed, the passivation mechanism remains the same in any solution containing 5 to 100 vol% water (25).

In the case of recirculating systems, using solutions containing oxygen purgers as inhibitors, care should be taken to keep the solution free of suspended particles, as this could impinge the surface of film exposing the substrate making more corrosion possible.

2. SEALANTS

In tests with denatured ethanol, most of the sealants provided exhibited an egregious performance. Sealants containing, isopropyl alcohol group and wood based resin exhibited good performance in terms of both leakage and solution color change. Presuming that these sealants have the same alcohol ring structure, they harden by cross linking into a three dimensional network. The time interval for cross linking referred to as "potlife" can vary depending on the reinforcement and fillers added as compounding agents.

Degradation in color of the test solution could be due to either loss of pigmentation used in the sealant or due to deterioration of the sealant itself. The loss of color or deterioration is predominantly true of the low recovery sealants with little or no crosslinking. This may be attributed to the fact that chemical reactions with sealant material takes place at a higher rate in the soft state than when hard.

Hence based on color change and leakage, isopropyl alcohol based sealants which hardened in two weeks on exposure to air seem to perform satisfactorily in the tested conditions.

3. ELASTOMERS

As is evident from the results, no physical changes were observed in the three rubber hoses. The solution color change to yellow is presumably due to the dissipation of sulfur into the solution. The reddish or orange tinge to the solution is the possible dissipation of the pigment from the rubbers. Studies have been conducted on various rubbers and their compatibility with gasoline and alcohols with the emergence of gasohols. It was found that polar rubbers were susceptible to deterioration in non polar liquids and vice versa, hence care is to be taken regarding the polarity (45). Since there was no deterioration detectable in the form of softening or swelling, which could mean bonding failure, no problem is foreseen with their use in heat pumps.

4. SOLDERS

In the study conducted by Nayak(8) and Pai(46), on various solders in potassium acetate based solution there was no attack except for deposition on the solder joints. In this study test conducted on conventional tin-lead solders revealed no attack. The results of tests on lead free solders was encouraging as there were no traces of corrosion or deposition.

CHAPTER VI

CONCLUSIONS

The following conclusions have been reached in this study, conducted to evaluate the material compatibility of Ground Source Heat pumps using ethanol based heat transfer fluids.

1. Though stainless steel is prone to SCC in pure chemical grade denatured ethanol, it does not exhibit any attack in diluted systems or in pure ethanol. Hence, stainless steel should not pose any problems in service with ethanol based antifreezes under any conditions that are anticipated in the heat pump systems.

2. Yellow brass does not show any significant corrosion problems. Some etching and crevice corrosion is observed under stagnant conditions. Since the fluid is not stagnant in the heat pump systems, substitution by the costlier red brass is not necessary.

3. Gray cast iron exhibits pitting and crevice corrosion, however the corrosion rate is uniform and low. Cast iron is expected to give a good service in GSHP systems using ethanol based antifreezes.

4. The rubber hoses, "Yeoman", "Wildfire", and the "Red rubber" hoses did not show any signs of swelling, dissolution and change in appearance or feel under constant immersion in test solutions. Some sulfur diffuses out of the hoses, initially but is not expected to cause in any problem with the working of the pumps. Care should be taken to confirm that non polar elastomers are used.

5. Of the twelve sealants tested, isopropyl alcohol based, high recovery sealants (Jomar green and Hercules Pro-dope) exhibit good resistance to pure and denatured ethanols and maybe preferred over the others for use in ethanol based systems.

6. Common lead-tin solders, and two of the commercial lead free solders did not show any attack or deposition and could be safely used in the heat pump systems using ethanol based antifreezes.

7. Many literature sources cited are in agreement that polyethylene, the buried loop material, will not be affected by ethanol.

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APPENDIX

SECTION I - NAME AND PRODUCT

MFG NAME AND ADDRESS
EM SCIENCES /MCB
P.O. BOX 5018

CHERRYHILL
NJ 080340395

CHEMICAL NUMBER: MEX0280-3
ITEM NUMBER : 489575
VNDR CATLG NBR :
ENTRY DATE : 08-15-85
CHANGE DATE : 11-25-85
EMERGENCY PHONE: 609 3549200

CHEMICAL NAME :
ETHYL ALCOHOL 95% DENAT 8.0 PT
TRADE NAME SYN :
ETHANOL
CHEMICAL FAMILY :
ALCOHOL

SECTION II - HAZARDOUS INGREDIENTS

HAZARDOUS COMPONENTS:
REFER TO SECTION 4-9

COMPONENT	APPROX. %	TLV
ETHANOL	87	1000 PPM
METHANOL	5	200 PPM
ETHYL ACETATE	1	400 PPM
METHYL ISO-BUTYL KETONE	1	100 PPM
HYDROCARBON SOLVENT	1	
WATER	BALANCE	

SECTION III - PHYSICAL DATA S/10 = SEE SECTION X

BOIL. POINT	SPECIFIC GRAVITY	VAPOR PRESS.	MELT. POINT	VAPOR DENSITY	EVAP. RATE	SOLUBLE IN WATER	PERCENT VOLATILE
79.4C	0.81	40	N/A	1.59	3.3 BUTYL ACETATE	MISCIB	100

APPEARANCE AND ODOR:
CLEAR, COLORLESS LIQUID, CHARACTERISTIC ODOR.

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT:	57 DEG. F. (CC)
FLAMMABLE LEL:	3.3 (ETHANOL)
FLAMMABLE UEL:	19.0 (ETHANOL)

EXTINGUISHING MEDIA:
DRY CHEMICAL, CO2, OR ALCOHOL FOAM
WATER SPRAY TO COOL FIRE-EXPOSED CONTAINERS & DISPERSE VAPORS.
SPECIAL FIRE FIGHTING PROCEDURES:
WEAR SELF-CONTAINED BREATHING APPARATUS

UNUSUAL FIRE AND EXPLOSION HAZARDS:
HIGHLY FLAMMABLE LIQUID.

SECTION V - HEALTH HAZARD DATA

THRESHOLD-LIMIT-VALUE:

OSHA STD-AIR: TWA 1000 PPM TXDS: ORL-HMN LDLO: 500 MG/KG
ORL-WMN TDLO: 256 GM/KG/12W*

EFFECTS OF OVEREXPOSURE:

POISON! CAUSES BLINDNESS AND DEATH ON INGESTION. EYE IRRITATION ON CONTACT; MAY DEFAT SKIN AFTER PROLONGED CONTACT. INHALATION IS NARCOTIC IN HIGH CONCENTRATIONS, CAUSING HEADACHE AND DIZZINESS.
TOXIC EFFECTS ON ENDOCRINE GLANDULAR SYSTEM

EMERGENCY AND FIRST AID PROCEDURES:

GET MEDICAL ASSISTANCE FOR ALL CASES OF OVEREXPOSURE. EYES: FLUSH WITH WATER 15 MINUTES; GET MEDICAL ASSISTANCE. SKIN: FLUSH WITH WATER; WASH THOROUGHLY WITH SOAP AND WATER. INHALATION: REMOVE TO FRESH AIR; GET MEDICAL ASSISTANCE. INGESTION: DRINK 1 OR 2 GLASSES OF WATER AND INDUCE VOMITING IF CONSCIOUS; GET MEDICAL ASSISTANCE.

SECTION VI - REACTIVITY DATA

INDICATORS: STABILITY - STABLE POLYMERIZATION - MAY NOT OCCUR

CONDITIONS TO AVOID:

HEAT, SPARKS, OPEN FLAME

INCOMPATIBILITY (MATL TO AVOID):

OXIDIZERS, CONCENTRATED NITRIC AND SULFURIC ACIDS, ALDEHYDES, HALOGENS AND THEIR COMPS .

HAZARDOUS DECOMPOSITION OR BY PRODUCTS:

COX

POLYMERIZATION CONTIONS TO AVOID:

N/A

SECTION VII - SPILL OR LEAK PROCEDURES OR DISPOSAL

MATERIAL RELEASE OR SPILL PROCEDURES:

ELIMINATE IGNITION SOURCES. FLUSH WITH WATER.

WASTE DISPOSAL METHOD:

TO BE PERFORMED IN COMPLIANCE WITH ALL CURRENT LOCAL, STATE, AND FEDERAL REGULATIONS.

ETHYL ALCOHOL USP - 200 PROOF

AAPER MSDS NUMBER: 100-A EFFECTIVE DATE: JANUARY 1, 1991

AAPER Alcohol and Chemical Company
P.O. Box 339, 11 Isaac Shelby Drive
Shelbyville, Kentucky 40066-0339
Telephone: (502) 633-0650

24 Hour Emergency Assistance: Chemtrec 1-800-424-9300

AAPER Alcohol and Chemical Company urges the customer receiving this Material Safety Data Sheet (MSDS) to study it carefully to become aware of hazards, if any, of the product involved. In the interest of safety, you should: (1) Notify your employees, agents, contractors of the information on this sheet, (2) Furnish a copy to each of your customers to inform their employees and customers as well.

SECTION I - IDENTIFICATION

PRODUCT NAME:	Alcohol USP, Ethyl Alcohol, 200 proof
SYNONYMS:	Anhydrous Ethyl Alcohol, Dehydrated Alcohol
CHEMICAL FAMILY:	Alcohol
MOLECULAR WEIGHT:	46.07
FORMULA:	C_2H_5OH

SECTION II - INGREDIENTS

COMPOSITION	CAS RN.	NOMINAL WT/WT%	PEL/TLV	HAZARD
Ethyl Alcohol	64-17-5	100.0	1000 ppm	Flammable/Nervous System Depressant

SECTION III - HEALTH INFORMATION

INHALATION:	Exposure to over 1000 ppm may cause headache, drowsiness and lassitude, loss of appetite, and inability to concentrate. Irritation of the throat.
INGESTION:	Can cause depression of central nervous system, nausea, vomiting, diarrhea.
EYE CONTACT:	Liquid or vapor may cause irritation.
SKIN CONTACT:	May cause irritation and defatting of skin on prolonged contact.

SECTION IV - OCCUPATIONAL EXPOSURE LIMITS

PEL (OSHA Permissible Exposure Limit):	Mixture - See Section II
TLV (ACGIH Threshold Limit Value):	Mixture - See Section II

SECTION V - EMERGENCY FIRST AID PROCEDURE

FOR OVEREXPOSURE BY:

SWALLOWING:	If victim is conscious and able to swallow, have victim drink water or milk to dilute. Never give anything by mouth if victim is unconscious or having convulsions. CALL A PHYSICIAN OR CHEMTREC (POISON CONTROL) IMMEDIATELY. Induce vomiting only if advised by physician or Chemtrec (Poison Control).
INHALATION:	Immediately remove victim to fresh air. If victim has stopped breathing, give artificial respiration, preferable mouth-to-mouth. GET MEDICAL ATTENTION IMMEDIATELY.
CONTACT WITH EYES OR SKIN:	Immediately flush affected area with plenty of cool water. Eyes should be flushed for at least 15 minutes. Remove and wash contaminated clothing before reuse. GET MEDICAL ATTENTION IMMEDIATELY.

SECTION VI - PHYSICAL DATA

BOILING POINT:	173°F
MELTING POINT:	-173°F
VAPOR PRESSURE:	44.6 mm Hg @ 68° F
SPECIFIC GRAVITY:	0.794 @ 60°/60°F
VAPOR DENSITY (AIR=1):	1.59
SOLUBILITY IN WATER:	Complete
APPEARANCE AND COLOR:	Clear and colorless

SECTION VII - FIRE AND EXPLOSION HAZARDS

FLASH POINT: 57°F ASTM D-56 (Tag Closed Cup)
AUTO-IGNITION TEMPERATURE: 685°F
FLAMMABLE LIMITS IN AIR, % BY VOL.: LOWER: 3.3 UPPER: 19
NFPA (NATIONAL FIRE PROTECTION ASSOCIATION) RATING: HEALTH (0) FIRE (3) REACTIVITY (0)
(Does not apply to exposure hazards other than during a fire.)

SECTION VIII- SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION:
WEAR FRESH AIR MASK IN CONFINED AREAS.
VENTILATION - LOCAL:
PROVIDE ADEQUATE LOCAL EXHAUST VENTILATION.
VENTILATION - MECHANICAL:
PROVIDE ADEQUATE GENERAL MECHANICAL VENTILATION.
VENTILATION - SPECIAL:
N/A
OTHER
USE IN HOOD
PROTECTIVE GLOVES:
SAFETY GLOVES
EYE PROTECTION:
SAFETY GOGGLES

SECTION IX - SPECIAL PRECAUTIONS

HANDLING AND STORAGE PRECAUTIONS:
KEEP CONTAINER CLOSED. AND PROTECTED FROM PHYSICAL DAMAGE. STORE IN A COO
WELL VENTILATED AREA, AWAY FROM SOURCES OF IGNITION. DO NOT TAKE INTERNAL
DO NOT GET IN EYES. AVOID PROLONGED OR REPEATED BREATHING OF VAPOR OR
CONTACT WITH SKIN. WASH THOROUGHLY AFTER HANDLING.

SECTION X - OTHER INFORMATION

NFPA 704:	0	3	0
	HEALTH	FLAMMABILITY	REACTIVITY

CANNOT BE MADE NON-POISONOUS!

NOTE: NA OR N/A DENOTES NOT-AVAILABLE OR NON-APPLICABLE

FIRE FIGHTING PROCEDURES: (Note: Individuals should perform only those fire-fighting procedures for which they have been trained.) Use dry chemical, "alcohol" foam, or carbon dioxide; water may be ineffective, but water should be used to keep fire-exposed containers cool. If a leak or spill has not ignited, use water spray to disperse the vapors and to protect men attempting to stop a leak. Water spray may be used to flush spills away from exposures and to dilute spills to nonflammable mixtures (NFPA-49 1975).

UNUSUAL FIRE & EXPLOSION HAZARDS: Firefighters should wear self-contained breathing apparatus in the positive pressure mode with a full face piece when there is a possibility of exposure to smoke, fumes, or hazardous decomposition products.

SECTION VIII - REACTIVITY

STABILITY: Generally stable.
HAZARDOUS POLYMERIZATION: Not likely.
CONDITIONS & MATERIALS TO AVOID: Contact with acetyl chloride and a wide range of oxidizing agents may react violently.

SECTION IX - EMPLOYEE PROTECTION

CONTROL MEASURES: Handle in the presence of adequate ventilation.

RESPIRATORY PROTECTION: Where exposure is likely to exceed acceptable criteria, use NIOSH/MSHA approved respiratory protection equipment. Respirators should be selected based on the form and concentration of contaminant in air and in accordance with OSHA (29 CFR 1910.134).

PROTECTIVE CLOTHING: Wear gloves and protective clothing which are impervious to the product for the duration of the anticipated exposure if there is potential for prolonged or repeated skin contact.

EYE PROTECTION: Wear safety glasses meeting the specifications of ANSI Standard Z87.1 where no contact with the eye is anticipated. Chemical safety goggles meeting the specifications of ANSI Standard Z87.1 should be worn whenever there is the possibility of splashing or other contact with the eyes.

SECTION X - ENVIRONMENTAL PROTECTION

ENVIRONMENTAL PRECAUTIONS: Avoid uncontrolled releases of this material. Where spills are possible, a comprehensive spill response plan should be developed and implemented.

SPILL OR LEAK PROCEDURES: Wear appropriate respiratory protection and protective clothing as described in Section IX. Contain spilled material. Transfer to secure containers. Where necessary, collect using absorbent media. In the event of an uncontrolled release of this material, the user should determine if the release is reportable under applicable laws and regulations.

WASTE DISPOSAL: All recovered material should be packaged, labeled, transported, and disposed of, or reclaimed in conformance with applicable laws and regulations and in conformance with good engineering practices.

SECTION XI - REGULATORY CONTROLS

DEPARTMENT OF TRANSPORTATION (DOT):

DOT CLASSIFICATION: Flammable Liquid
DOT PROPER SHIPPING NAME: Ethyl Alcohol
OTHER DOT INFORMATION: Identification No. UN1170
Emergency Response Guide No. 26

ATF DISTILLED SPIRITS ACT: Use of ethyl alcohol without prior payment of applicable excise tax is strictly controlled by regulations promulgated and enforced by the Bureau of Alcohol, Tobacco, and Firearms (ATF), Department of the Treasury. Governing regulations have been defined in Title 27, Code of Federal Regulations.

TOXIC SUBSTANCE CONTROL ACT (TSCA): This product is listed in the TSCA Inventory of Chemical Substances.

SECTION XII - PRECAUTIONS: HANDLING, STORAGE AND USAGE

Protect container against physical damage. Detached or outside storage is preferred. Inside storage should be in a NFPA approved flammable liquid storage room or cabinet. All ignition sources should be eliminated. Smoking should be prohibited in storage areas. Electrical installations should be in accordance with Article 501 of the National Electrical Code. NFPA 30, Flammable and Combustible Liquids Code, should be followed for all storage and handling. Frequent careful leakage inspections should be done. Automatic sprinkler system should be provided. Isolate from oxidizers, chemicals capable of spontaneous heating, materials reacting with air or moisture to liberate heat, ignition sources and explosives. Consult local fire codes for additional storage information.

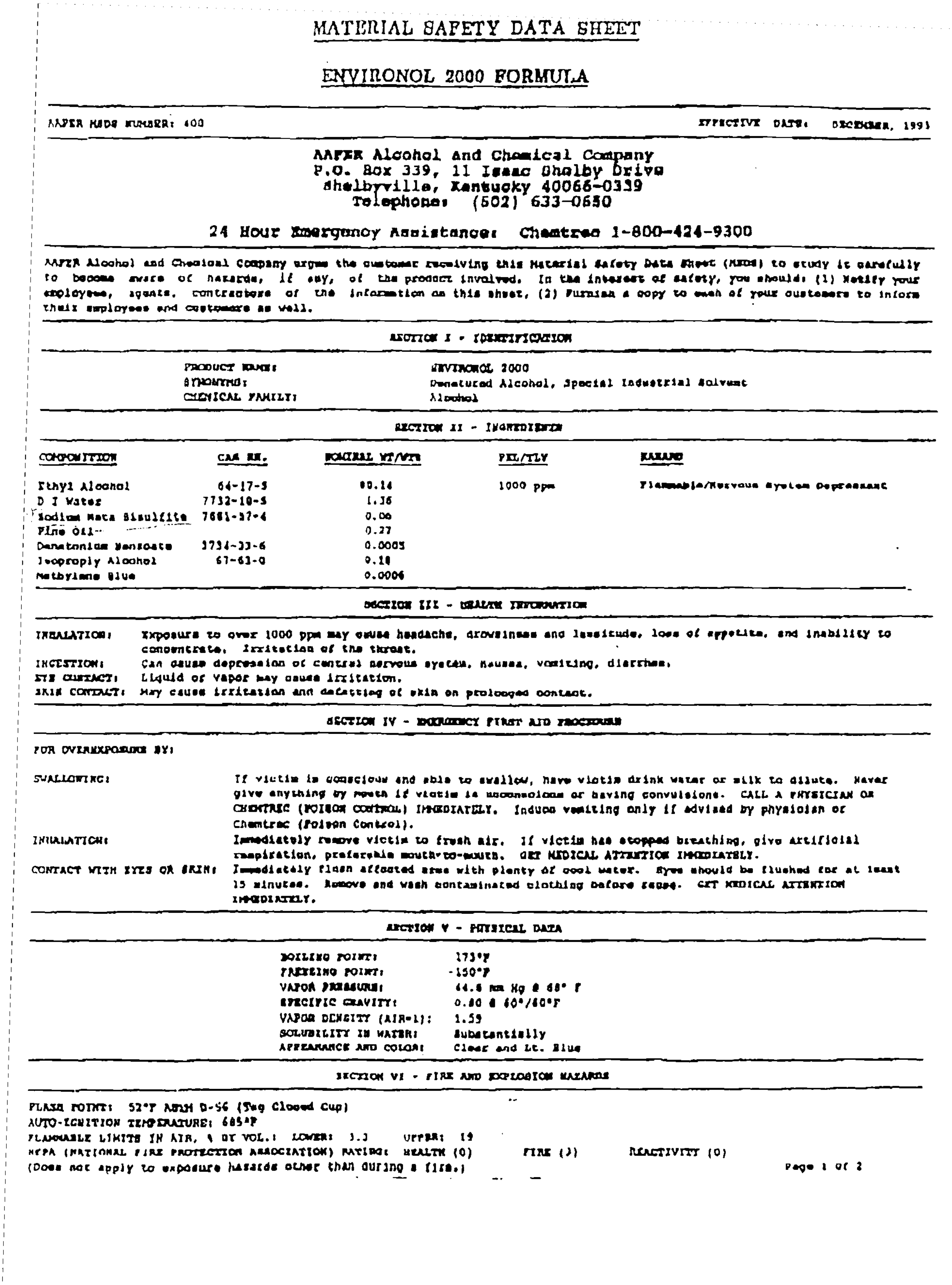
When contents are being transferred, the metallic container must be bonded to the receiving container and grounded to avoid static discharges. Never use pressure to empty. Replace closure securely after each opening.

Keep material packaged in drums or bottles out of sun and away from heat. Remove closure carefully; internal pressure may be present. Keep closure on to prevent leakage.

Container hazardous when empty. Since emptied containers retain residual product (vapor and liquid), all precautions described on this MSDS must be observed.

CAUTION: For manufacturing, processing, repackaging, or industrial use. Not for household use.

The information contained herein is furnished without warranty of any kind. Employers should use this information only as a supplement to other information gathered by them and must conduct testing and/or make independent determinations of suitability and completeness of information from all sources to assure proper use of these materials and the safety and health of employees.



MATERIAL SAFETY DATA SHEET

ENVIRONOL 2000 FORMULA

AAPER MSDS NUMBER: 400 EFFECTIVE DATE: DECEMBER, 1993

AAPER Alcohol And Chemical Company
P.O. Box 339, 11 Isaac Shelby Drive
Shelbyville, Kentucky 40066-0339
Telephone: (502) 633-0650

24 Hour Emergency Assistance: Chemtrec 1-800-424-9300

AAPER Alcohol and Chemical Company urges the customer receiving this Material Safety Data Sheet (MSDS) to study it carefully to become aware of hazards, if any, of the product involved. In the interest of safety, you should: (1) Notify your employees, agents, contractors of the information on this sheet, (2) Furnish a copy to each of your customers to inform their employees and customers as well.

SECTION I - IDENTIFICATION

PRODUCT NAME: ENVIRONOL 2000
SYNONYMS: Denatured Alcohol, Special Industrial Solvent
CHEMICAL FAMILY: Alcohol

SECTION II - INGREDIENTS

COMPOSITION	CAS NR.	NOMINAL WT/WT%	PEL/TLV	HAZARD
Ethyl Alcohol	64-17-5	90.14	1000 ppm	Flammable/Nervous System Depressant
D I Water	7732-18-5	1.36		
Sodium Meta Bisulfite	7681-57-4	0.06		
Pine Oil		0.27		
Denatonium Benzoate	3734-33-6	0.0005		
Isoproply Alcohol	67-63-0	9.18		
Methylene Blue		0.0006		

SECTION III - HEALTH INFORMATION

INHALATION: Exposure to over 1000 ppm may cause headache, drowsiness and lassitude, loss of appetite, and inability to concentrate. Irritation of the throat.
INGESTION: Can cause depression of central nervous system, nausea, vomiting, diarrhea.
EYE CONTACT: Liquid or vapor may cause irritation.
SKIN CONTACT: May cause irritation and defatting of skin on prolonged contact.

SECTION IV - EMERGENCY FIRST AID PROCEDURES

FOR OVEREXPOSURE BY:

SWALLOWING: If victim is conscious and able to swallow, have victim drink water or milk to dilute. Never give anything by mouth if victim is unconscious or having convulsions. CALL A PHYSICIAN OR CHEMTREC (POISON CONTROL) IMMEDIATELY. Induce vomiting only if advised by physician or Chemtrec (Poison Control).

INHALATION: Immediately remove victim to fresh air. If victim has stopped breathing, give artificial respiration, preferably mouth-to-mouth. GET MEDICAL ATTENTION IMMEDIATELY.

CONTACT WITH EYES OR SKIN: Immediately flush affected area with plenty of cool water. Eyes should be flushed for at least 15 minutes. Remove and wash contaminated clothing before reuse. GET MEDICAL ATTENTION IMMEDIATELY.

SECTION V - PHYSICAL DATA

BOILING POINT: 173°F
FREEZING POINT: -150°F
VAPOR PRESSURE: 44.6 mm Hg @ 68° F
SPECIFIC GRAVITY: 0.80 @ 60°/60°F
VAPOR DENSITY (AIR=1): 1.59
SOLUBILITY IN WATER: Substantially
APPEARANCE AND COLOR: Clear and Lt. Blue

SECTION VI - FIRE AND EXPLOSION HAZARDS

FLASH POINT: 52°F ASTM D-56 (Tag Closed Cup)
AUTO-IGNITION TEMPERATURE: 685°F
FLAMMABLE LIMITS IN AIR, % BY VOL.: LOWER: 3.3 UPPER: 19
NFPA (NATIONAL FIRE PROTECTION ASSOCIATION) RATING: HEALTH (0) FIRE (3) REACTIVITY (0)
(Does not apply to exposure hazards other than during a fire.)

FIRE FIGHTING PROCEDURES: (Note: Individuals should perform only those fire-fighting procedures for which they have been trained.) Use dry chemical, "alcohol" foam, or carbon dioxide; water may be ineffective, but water should be used to keep fire-exposed containers cool. If a leak or spill has not ignited, use water spray to disperse the vapors and to protect men attempting to stop a leak. Water spray may be used to flush spills away from exposures and to dilute spills to nonflammable mixtures (NFPA-49 1991).

UNUSUAL FIRE & EXPLOSION HAZARDS: Firefighters should wear self-contained breathing apparatus in the positive pressure mode with a full face piece when there is a possibility of exposure to smoke, fumes, or hazardous decomposition products.

SECTION VII - REACTIVITY

STABILITY: Generally stable.

HAZARDOUS POLYMERIZATION: Not likely.

CONDITIONS & MATERIALS TO AVOID: Contact with acetyl chloride and a wide range of oxidizing agents may react violently.

SECTION VIII - EMPLOYEE PROTECTION

CONTROL MEASURES: Handle in the presence of adequate ventilation.

RESPIRATORY PROTECTION: Where exposure is likely to exceed acceptable criteria, use NIOSH/MSHA approved respiratory protection equipment. Respirators should be selected based on the form and concentration of contaminant in air and in accordance with OSHA (29 CFR 1910.134).

PROTECTIVE CLOTHING: Wear gloves and protective clothing which are impervious to the product for the duration of the anticipated exposure if there is potential for prolonged or repeated skin contact.

EYE PROTECTION: Wear safety glasses meeting the specifications of ANSI Standard Z87.1 where no contact with the eye is anticipated. Chemical safety goggles meeting the specifications of ANSI Standard Z87.1 should be worn whenever there is the possibility of splashing or other contact with the eyes.

SECTION IX - ENVIRONMENTAL PROTECTION

ENVIRONMENTAL PRECAUTIONS: Avoid uncontrolled releases of this material. Where spills are possible, a comprehensive spill response plan should be developed and implemented.

SPILL OR LEAK PROCEDURES: Wear appropriate respiratory protection and protective clothing as described in Section IX. Contain spilled material. Transfer to secure containers. Where necessary, collect using absorbent media. In the event of an uncontrolled release of this material, the user should determine if the release is reportable under applicable laws and regulations.

WASTE DISPOSAL: All recovered material should be packaged, labeled, transported, and disposed of, or reclaimed in conformance with applicable laws and regulations and in conformance with good engineering practices.

SECTION X - REGULATORY CONTROLS

DEPARTMENT OF TRANSPORTATION (DOT):

DOT CLASSIFICATION: Flammable Liquid

DOT PROPER SHIPPING NAME: Denatured Alcohol

OTHER DOT INFORMATION: Identification no. NA1986
Emergency Response Guide No. 26

ATF DISTILLED SPIRITS ACT: Use of ethyl alcohol without prior payment of applicable excise tax is strictly controlled by regulations promulgated and enforced by the Bureau of Alcohol, Tobacco, and Firearms (ATF), Department of the Treasury. Governing regulations have been defined in Title 27, Code of Federal Regulations.

TOXIC SUBSTANCE CONTROL ACT (TSCA): This product is listed in the TSCA Inventory of Chemical Substances.

SECTION XI - PRECAUTIONS: HANDLING, STORAGE AND USAGE

Protect container against physical damage. Detached or outside storage is preferred. Inside storage should be in a NFPA approved flammable liquid storage room or cabinet. All ignition sources should be eliminated. Smoking should be prohibited in storage areas. Electrical installations should be in accordance with Article 501 of the National Electrical Code. NFPA 30, Flammable and Combustible Liquids Code, should be followed for all storage and handling. Frequent careful leakage inspections should be done. Automatic sprinkler system should be provided. Isolate from oxidizers, chemicals capable of spontaneous heating, materials reacting with air or moisture to liberate heat, ignition sources and explosives. Consult local fire codes for additional storage information.

When contents are being transferred, the metallic container must be bonded to the receiving container and grounded to avoid static discharges. Never use pressure to empty. Replace closure securely after each opening.

Keep material packaged in drums or bottles out of sun and away from heat. Remove closure carefully; internal pressure may be present. Keep closure on to prevent leakage.

Container hazardous when empty. Since emptied containers retain residual product (vapor and liquid), all precautions described on this MSDS must be observed.

CAUTION: For manufacturing, processing, repackaging, or industrial use. Not for household use.
The information contained herein is furnished without warranty of any kind. Employees should use this information only as a supplement to other information gathered by them and must conduct testing and/or make independent determinations of suitability and completeness of information from all sources to assure proper use of these materials and the safety and health of employees.

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