

Metallic materials compatibility in E22 and M15 motor fuel blends

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Factors influencing the potential corrosiveness of E22 and M15 motor fuels were studied using immersion and electrochemical corrosion tests. The latter were carried out using fuels at 18 °C and 50 °C with and without additions of water contaminants (inorganic acids, chloride ions, and salts).

The corrosion behaviour of carbon steels (St 52, 100Cr6), stainless steels (AISI 304, AISI 440 C) and aluminium alloys (AlMg3, 6056 aluminium alloy) was evaluated.

AISI 304 was fully compatible either in as-received or modified fuels in all experimental conditions here imposed. AISI 440 C steel was able to develop a homogeneous passive film when was exposed at 18 °C, but a loss of corrosion resistance was detected when the temperature raised to 50 °C. Aluminium alloys were the poorest performers in these fuels, exhibiting significant damaging under the form of surface pitting.

Carbon steels exhibited reasonable resistances only in E22 and M15 fuels at 18 °C.

KEYWORDS:

steel, aluminum and aluminum alloy, corrosion

INTRODUCTION

The use of alcohols as transportation fuels is rapidly increasing because they can be obtained from different and widespread resources and because of the potential abatement of environmental pollution [1]. Most current production of methanol is from natural gas feedstock, and ethanol from fermentation of sugar and grain crops. Nevertheless, methanol can be also produced using coal, cellulosic refuse and biomass and all these possible sources are more uniformly distributed around the globe than petroleum resources. By this way, the automotive industry is interested to develop vehicles compatible with mixtures of gasoline with methanol or ethanol.

When ethanol is produced by biomass fermentation, it is hydrated with about 5% water. Recently, it has become practical to produce alcohol with less than 0.1% water at acceptable cost for blending with petrol, [2]. This is important, since the solubility of ethanol and methanol in gasoline in the presence of even a small quantity of water is very limited. The amount of water that can be tolerated by a 25% ethanol/gasoline blend at room temperature is about 1%, and larger water additions would rapidly cause phase separation: alcohol will rapidly separate from the gasoline and settle to the bottom of the container. For methanol, the presence of water is even a more serious problem. The addition of higher alcohols (such as iso-propanol, 1-butanol or n-decanol) as co-solvents counteracts phase separation, [3].

The largest demonstration of ethanol as a motor vehicle fuel is in Brazil where, since '90s, about 40% of vehicles operate with E100 (95% ethanol, 5% water) and 60% with E22 (78% gasoline, 22% ethanol), [4]. These blends both require specific vehicle op-

timisations (re-calibration and component changes).

In U.S.A., General Motors first developed the so-called Variable Fuel Vehicles (VFV), which can operate with any mixture of methanol and gasoline up to M85 (85% by volume of methanol) or, alternatively, with ethanol-gasoline blends up to Ed85 (85% by volume of ethanol, which is denatured by addition of hydrocarbons at a concentration of about 5% by volume). However, ethanol is more used to formulate E10 (gasohol, 10% ethanol by volume), which does not impose specific technologies. The finished product must conform to gasoline specified by ASTM D 4814-88 and a waiver can be granted for an oxygenated 'recipe' that is demonstrated not to cause or contribute to the failure of any emission control device or system, [5]. The significant corrosiveness of ethanol/methanol fuels impose quality control of their constitution, limits on acidity, sulphur and chlorine in alcohol fuels are indicated in both ASTM and California Air Resources Board (CARB) specifications [6]. For M85 and E85, even more restrictive specifications have been advocated by General Motors (GM) with the aim to improve vehicle performance and durability, [7,8]. Key features included a Cold Starting Performance Index to improve wintertime starting, a conductivity and chloride ion specification to reduce corrosion, and a particulate contamination limit to reduce filter plugging.

In Europe, the ethanol limit is controlled by the oxygen content limit of 2.7%, which correspond to an ethanol limit of 7.8%. No waiver for ethanol blends higher than 7.8% is provided, [1].

Another possibility for use of methanol and ethanol in transportation fuels is as feedstock for methyl- and ethyl-tertiarybutyl ether (MTBE and ETBE) production, which exhibit favourable motor fuel characteristics and could be used for reformulated gasolines (more environmental benign than conventional gasolines) to achieve required oxygen and octane levels.

Alcohol motor fuels have been demonstrated to induce many problems of material compatibility, giving effects on vehicle driveability and durability. Both metallic and non metallic materials in the fuel distribution, storage and dispensing systems can suffer problems when exposed to alcohols, either neat or in blends. The corrosiveness of alcohols towards metallic materials can be

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increased by the presence of dissolved water and contaminants, [9,10,11,12,13]. Moreover, alcohols are better electric conductors than gasoline, and they can promote galvanic corrosion. Many fuel systems are fabricated from plastics and soft, flexible elastomers and the solvent power of alcohols may induce swelling, softening and loss of tensile strength; plastics or fibre glass can weaken, become brittle and crack or leak, [14].

Additional problems can be created by the peculiar physicochemical properties of alcohols. For instance, despite their relatively low molecular weights, methanol and ethanol fuels each have a lower Reid Vapour Pressure (RVP, vapour pressure at 100 °F) than those typical of gasoline (this is because of the molecular attractive forces resulting from relatively higher polarities). By this way, the low vapour pressure of neat or near-neat alcohols can create a cold-start difficulty for engines at low ambient temperatures.

The field of interest of the present study was restricted to the compatibility of metallic materials used in fuel injection systems when in contact with E22 and M15 fuel mixtures. Static corrosion immersion tests and electrochemical studies were carried out in order to characterize the corrosion behaviour of materials and variables affecting corrosiveness of motor fuel blends. The service life of mechanical components is strongly affected by dynamic conditions of temperature, pressure and flow that occur in real vehicle usage. Nevertheless, from the experimental results here presented some generalizations can be made about the materials selection for service in E22 or M15 fuels.

MATERIALS AND METHODS

Tested fuels

The motor fuel blends used as base solutions for corrosion tests were E22 and M15 blends provisioned by ELF. These fuels will be hereinafter referred as Fuel1 and Fuel2 respectively. As shown in Table 1, five other fuels were prepared adding to Fuel1 and Fuel2 different amounts of water and acidic contaminants, with the aim to increase the corrosion potential. Fuels 3 and 5 were prepared adding to the as-received fuels 0.1% of distillate water, 3 ppm chloride ions and 60 ppm formic acid. Fuels 4 and 6 were obtained adding to the as-received fuels 0.25% distillate water, 3 ppm chloride ions and 60 ppm formic acid. Finally, Fuels 7 and 8 were prepared mixing 495 ml of alcohol-gasoline fuel to 495 ml of isopropyl-alcohol and 10 ml of hydrochloric acid (37%wt) in order to increase fuel conductivity up to 500 $\mu\text{S}/\text{cm}$. The following analyses have been carried out on test fuels:

pH: the fuels pH was measured with an HANNA pH-meter model 211 equipped with aqueous-non aqueous dual electrodes.

Water content: water contents were determined by titration with Karl-Fisher reagent using a Metrom apparatus, [15].

Total acidity: this measurement was carried out following ASTM D 664-89, "Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration". The fuel sample is added

to a solution of toluene, isopropyl-alcohol and water. The total acidity determination was carried out by potentiometric titration using an alcoholic solution of KOH, which was in turn characterised using an aqueous solution of Potassium hydrogen phthalate, [16].

Electrical conductivity: measurements were made with a METROM model 712 conductivity meter, equipped with a cell (N. 012001) designed for non-aqueous media. Readings were temperature compensated by the meter, [17].

Ion chromatography: this method was used to determine trace amounts of anions that might be associated with acidic contaminants in the fuels. The IC measurements were performed with a DIONEX model DX100, equipped with a column of separation AG4A-SC. The alcoholic-gasoline blends were mixed and stirred with an eluant in the ratio 200 ml/20 ml. The eluant was constituted of an aqueous solution 0.1 mM of $\text{NaH}(\text{CO}_3)$ and 0.1 mM of $\text{Na}_2(\text{CO}_3)$. The time given for phase separation was 48 hours. After extraction of the aqueous phase, for both fuels a pH value around 5 has been measured. The pH value of aqueous phases was increased to about 9 using solid pellets of NaOH. The solutions were dried at 200 °C within a sand bath. The residual was dissolved using an eluant and the organic constituents were destroyed at 100 °C with a microwave digester Mileston Model MLS-1200 Mega. The eluant was diluted with a ratio 1:10⁴. This solution was that used for IC analysis, [18].

Selected metals

Three different classes of metallic materials were chosen as they represent the most common metallic alloys used in fuel injection systems. They can be grouped as follows:

- Group 1: low carbon (St 52) and high carbon (100Cr6) steels,
- Group 2: martensitic (AISI 440C) and austenitic (AISI 304) stainless steels,
- Group 3: AlMg3 and 6056 aluminium alloy.

Immersion corrosion tests

The potential corrosiveness of as-received and modified fuels towards metallic materials has been evaluated carrying out immersion tests at two different temperatures of 18 °C (30-45 days of immersion) and 50 °C (45 days of immersion).

The experimental procedures adopted for corrosion testing followed the recommendations from ASTM G31, "Standard Practice for Immersion Corrosion Testing of Metals", [19,20]. Rectangular coupons 6.0x3.0x0.2 mm in dimensions have been used, except for 6056 aluminium alloy and AISI 440 C alloys. For 6056 aluminium alloy, a planar thick specimen was extracted from a fuel pump case, whereas AISI 440 C was only available under the form of cylindrical bars 8 cm in length and 8 mm in diameter. Before immersion, all specimens were cleaned, degreased with acetone, air dried and weighted using an analytical balance with accuracy of 10⁻⁵ g. For each series a number

Fuel	Base	H ₂ O content (vol %)	Cl- content (wt ppm)	HCOOH (vol ppm)	isopropyl alcohol (vol %)	HCl (vol %)
1	E22	–	–	–	–	–
2	M15	–	–	–	–	–
3	E22	0.1	3	60	–	–
4	E22	0.25	3	60	–	–
5	M15	0.1	3	60	–	–
6	M15	0.25	3	60	–	–
7	E22	–	–	–	49,5	1
8	M15	–	–	–	49,5	1

TAB. 1
Test fuels used for corrosion immersion tests.
Benzine usate per i test di corrosione per immersione.

from 2 to 5 of specimens, depending on alloy availability, were simultaneously tested. Before evaluation of the mass loss, the corrosion products were removed by acid pickling using a filming inhibitor to minimize further metal loss, [21]. Weight changes, microscopic inspection, and a photographic record of each specimen were noted.

Electrochemical tests

The corrosion behaviour of St52, AlMg3, AISI 304 and 100Cr6 alloys in as-received and modified M15 fuels have been evaluated using electrochemical techniques. Polarization curves have been obtained according to ASTM G5-94 Standard Practice: 'Standard Reference Test Method For Making Potentiostatic And Potentiodynamic Polarization Measurements', [22]. A three electrode standard electrochemical cell was used with double-junction calomel electrode. The Luggin capillary was filled with a LiCl saturated aqueous solution. No support electrolyte was used to increase conductivity of fuels. A Princeton Model 263A potentiostat equipped with a positive feedback circuit was used to compensate for the ohmic drop. The open circuit potentials were recorded after 1 hour of immersion and a scan rate of 0.16 mV/s was used to obtain relevant cathodic and anodic polarization curves. The corrosion potentials (E_{corr}) and corrosion rates (I_{corr}) have been determined using the Tafel extrapolation method (by using the software SoftCorr II®).

RESULTS AND DISCUSSION

Physical-chemical characteristics of tested Fuels

Table 2 summarizes physical-chemical measured characteristics of as-received E22 (Fuel1) and M15 (Fuel2). The low values of acidity and the relatively high fuels pH are apparent. Fuel2 (M15) exhibited the lowest water content (770 ppm) in correspondence of the highest conductivity (0.53 μ S/cm). The ion chromatograms showed only the presence of chloride and no evidence for sulphate ions or other anions.

The addition of 0.1% water containing acidic contaminants lowered the pH of both E22 and M15 fuels and determined significant increases of conductivity (Fuels 3 and 5 in Table 2). It can be observed that the addition of 0.25% water to fuel 2 (M15) led to some loss of conductivity (Fuel 6 in Table 2). This effect might be related to the occurrence of phase separation within the gasoline/methanol blend, although such an effect was not macroscopically evident.

Fuel 7 and Fuel 8 have been prepared respectively from Fuel 1 and Fuel 2 using additions of isopropyl alcohol and hydrochloric acid until the fuel conductivity raised to 500 μ S/cm. The pH

Fuel	pH	%H ₂ O	Acidity (mg KOH/g)	Conductivity (μ S/cm)	Cl ⁻ (ppm)
1	8.7	0.158	0.272	0.10	5.6
2	7.3	0.077	0.108	0.53	6.9
3	N.D	0.258	–	0.14	–
4	N.D.	0.408	–	0.19	–
5	5.4	0.177	–	0.9	–
6	5.4	0.327	–	0.31	–
7	0.7	–	–	500	–
8	0.7	–	–	500	–

TAB. 2 Results of analysis of Fuels used for corrosion immersion tests.

Risultati delle analisi delle benzine usate nei test di immersione.

value in both cases was lowered to 0.7 units. These last fuels were used only to evaluate the effect of fuel conductivity on the corrosion rates of materials in electrochemical tests.

Immersion tests

Table 3 summarizes experimental results obtained from corrosion immersion tests. The limited amount of E22 and M15 fuels provisioned for testing did not allow evaluating all materials in all experimental testing conditions, as shown in Table 3.

Concerning carbon steels, in spite of the difference in chemical composition and microstructure, the St52 (low carbon, ferritic-perlitic) and 100Cr6 (high carbon, tempered martensite) exhibited similar corrosion resistances in fuels 1/2/3/6 at 18 °C. When tested at 18 °C, the average corrosion rates were rather low in both Fuels 1 and 2, resulting always below 0.25 mdd. The additions of water and contaminants in Fuel 3 (E22 + 0.1% water + cont.) and Fuel 6 (M15 + 0.1% water + cont.) did not worsen significantly the corrosion resistance of St52 steel, at least when tested at 18 °C. On the contrary, when St52 was tested at 50 °C in Fuel 4 and contaminants were added to M15 (Fuel 3 and 6 in Table 2), a significant increase in the corrosion rates was observed (around 0.8 mdd), see Table 3.

The poor effect of water addition on the corrosion behaviour of the tested fuel could be explained by the absence of a phase separation. When in solution, the influence of water content is likely to be due to the formation of a chemiadsorbed monolayer phase on the metal surface [23, 14]. Water can act as an oxid-

Fuel	St52		100Cr6		AISI 304		AISI 440 C		AlMg3		6056 aluminium alloy	
	18 °C (mdd)	50 °C (mdd)	18 °C (mdd)	50 °C (mdd)								
1	0.13	0.20	0.13		0.05		0.03	0.40	2.70	3.00	3.50	
2	0.14		0.14		0.04		0.01		3.12		2.17	
3	0.12		0.12		0.01	<0.01	0.06		1.35	2.91	1.22	
4		0.75			<0.01	<0.01			1.71	1.65		
5									1.02			
6	0.16	0.75			0.01	0.01			1.60	1.13		

TAB. 3 Corrosion rates measured at 18 °C (30 days) and 50 °C (45 days) for different metallic materials exposed to as-received and modified E22 and M15 motor fuels. Corrosion rates are expressed in milligrams/dm²day (mdd).

Velocità di corrosione misurate a 18 °C (30 giorni) e 50 °C (45 giorni) per i differenti materiali metallici esaminati esposti alle benzine E22 e M15 tal quali e modificate. Le velocità di corrosione sono espresse in mg/dm²day (mdd).

zing agent, and its bulk concentration as well as its diffusion rate are important factors for corrosion of metals. When a phase separation occurs, aggressive species as salts (SO_4 , Cl) and organic acids (HCOOH , CH_3COOH) which are contained in petroleum distillates and industrial alcohols may be extracted and concentrated into the aqueous phase in contact with the metallic surface. In fact, increased corrosiveness and corrosion damage of storage tanks, pipelines, pumps and other equipments have been reported in literature [24, 25, 26, 27, 28].

Fig. 1 shows details of the corroded surface of St52 tested at 50 °C (45 days) in Fuel 5. It can be observed some degree of localisation of the corrosion damage, with formation of surface pits. The electron images in Figs. 2 a/b show evidence of preferential corrosion paths within the microstructure. Inside surface pits the grain boundaries become evident.

The corrosion resistance of stainless steels was rather different. The corrosion rates of austenitic SS AISI 304 were very low in all experimental conditions. The alloy was able to develop a rather protective and stable passive film in all test fuels. The corrosion resistance of martensitic SS AISI 440 C was high when exposed at 18 °C in both as-received fuels, with corrosion rates below

0.03 mdd, see Table 3. On the contrary, when the testing temperature was increased to 50 °C, the corrosion rate in Fuel 1 increased of an order of magnitude (0.4 mdd). The corrosion resistance of martensitic stainless steels is usually rather poor when compared to austenitic grades. This is because of the absence of nickel in the alloy and because of the highly deformed martensitic structure. Under these circumstances, one may speculate about the difficulty to sustain a continuous and stable passive film in these environments when the temperature is increased. The corrosion morphology appeared even in this case rather localized, see Fig.3.

Aluminium alloys were the poorest performers when in contact with alcohol-gasoline blends. Although the corrosion rates for 6056 aluminium alloy may suffer for some uncertainties due to the use of irregular shaped corrosion specimens, it seems that the corrosion behaviour is rather similar to that of AlMg3 alloy. For the latter, the average corrosion rate at 18 °C was 2.7 mdd in fuel 1 and 3.1 mdd in fuel 2, see Table 3. The addition of water, even containing acidic impurities was to some extent beneficial: the corrosion rates decrease to about 1.4 mdd in Fuel 3, 1.7 mdd in Fuel 4 and 1.6 mdd in Fuel 6. Increasing the test temperature

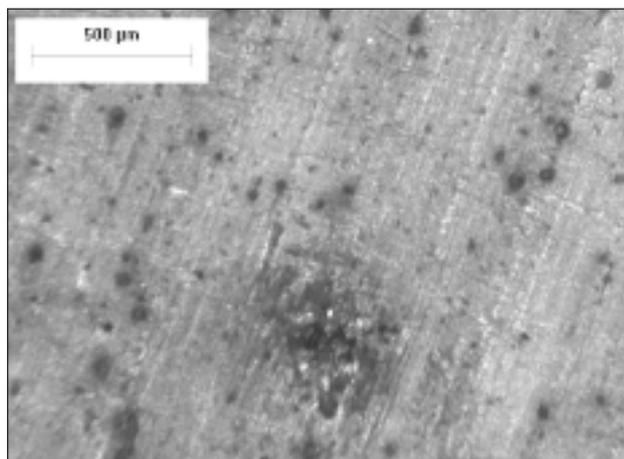


FIG. 1 Corroded surface of St52 steel tested at 50 °C (45 days) in fuel 5.

Superficie corrosa dell'acciaio St52 immerso a 50 °C (45 giorni) nella benzina 5.

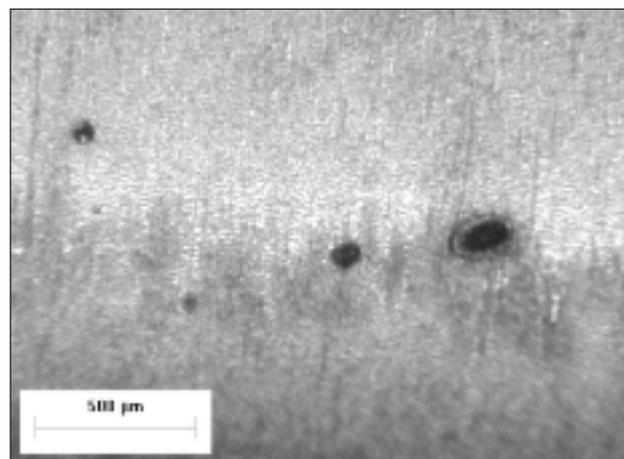


FIG. 3 Surface of AISI 440 steel after 30 days of immersion in Fuel 1 at 18 °C.

Superficie dell'acciaio AISI 440 dopo immersione per 30 giorni nella benzina 1 a 18 °C

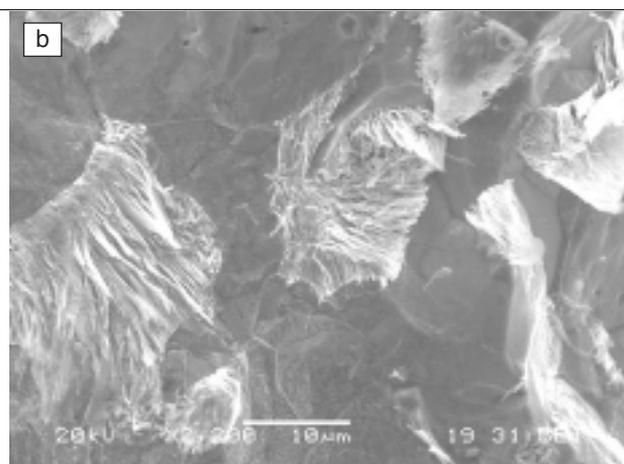
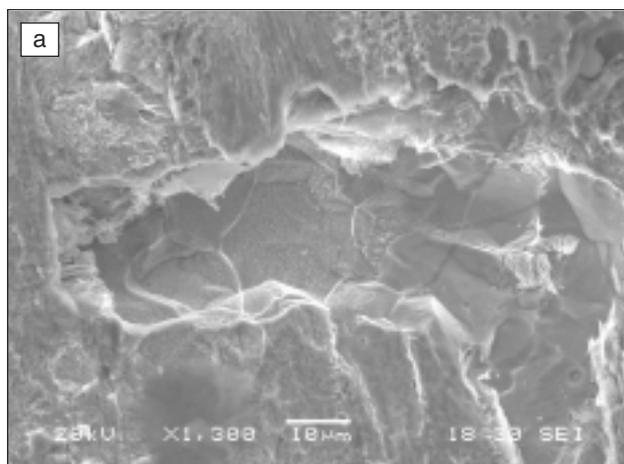


FIG. 2 a: Scanning electron micrography showing pits on St52 steel surface after 45 days of immersion in Fuel 1 at 50 °C; b: Scanning electron micrography showing pits on St52 steel surface after 30 days of immersion in Fuel 1 at 18 °C.

a: Micrografia SEM che mostra il pitting presente sulla superficie dell'acciaio St52 dopo 45 giorni di immersione nella benzina 1 a 50 °C; b: Micrografia SEM che mostra il pitting presente sulla superficie dell'acciaio St52 dopo 30 giorni di immersione nella benzina 1 a 18 °C.

Material	Fuel	O.C.P (mV/SCE)	E_{corr} (mV/SCE)	I_{corr} ($\mu\text{A}/\text{cm}^2$)
St52	2	-177	-188	0.13
St52	6	-137	35	5.62
St52	8	-365	-394	133.7
AlMg3	2	-711	-492	0.52
AlMg3	6	-615	-389	0.33
AlMg3	8	-755	-745	64.2
AISI 304	2	-109	-112	0.05
AISI 304	6	42	104	1.41
AISI 304	8	-328	-329	-
100Cr6	2	-264	-182	1.33
100Cr6	6	-115	-6	5.51
100Cr6	8	-350	-352	209.31

TAB. 4 Results from electrochemical tests.
Risultati delle prove elettrochimiche

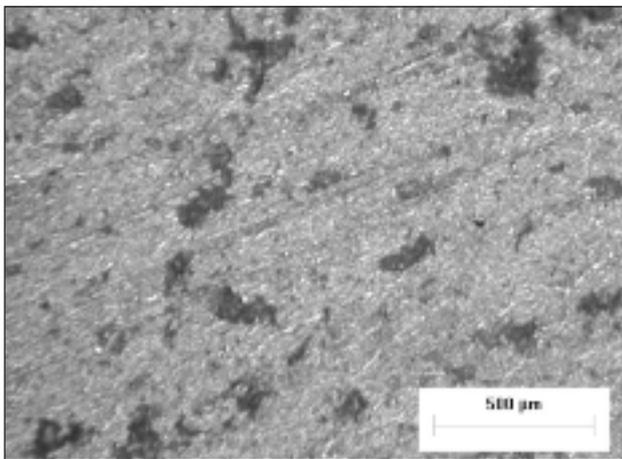


FIG. 4 Surface of AlMg3 aluminium alloy after 45 days of immersion in Fuel 4 at 18 °C.
Superficie della lega di alluminio AlMg3 immersione per 15 giorni nella benzina 4 a 18 °C.

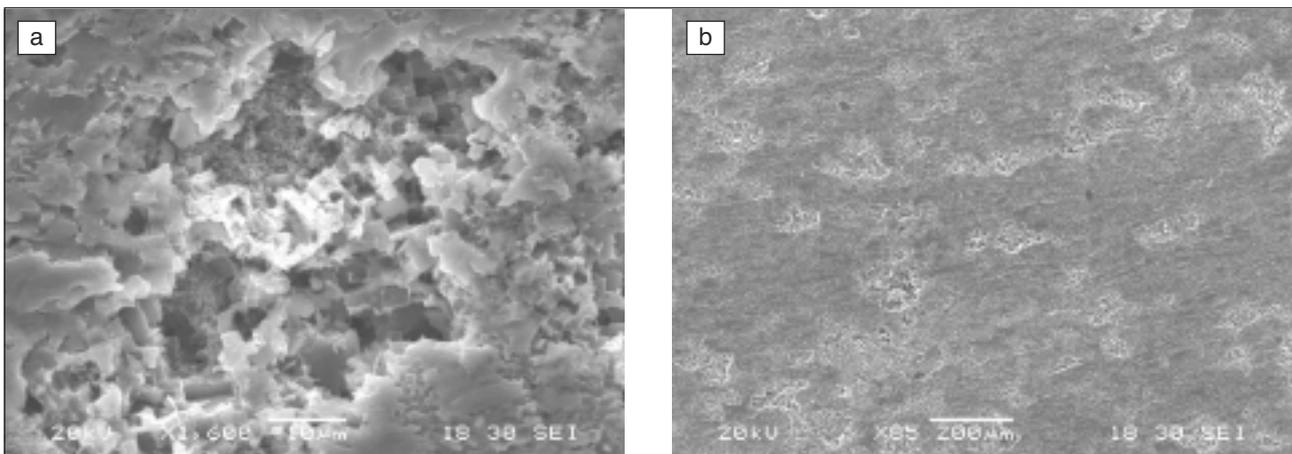


FIG. 5 Scanning electron micrographies showing pits on AlMg3 aluminium alloy surface after 45 days of immersion in Fuel 6 at 50 °C.
Micrografie SEM che mostrano il pitting presente sulla superficie della lega di alluminio AlMg3 dopo 45 giorni di immersione nella benzina 6 a 50 °C

seems to slightly increase corrosiveness of test fuels. The morphology of corrosive damage appeared localised. Fig.4 shows a low magnification image and Fig.5 shows details of corroded surfaces. Large surface roots were formed together with small sized surface pits.

Electrochemical tests

Table 4 summarises results obtained from the electrochemical tests. The Open Circuit Potentials (O.C.P) of materials are compared to Corrosion Potentials (E_{corr}), as determined using the Tafel extrapolation method from experimental polarization curves. OCP and E_{corr} values result very similar in Fuels 2 and 7. The difference registered for Fuel 6 can be attributed to water phase separation, which, as mentioned before, decreases solution conductivity.

The low conductivities of fuels caused difficulties in the relief of polarization curves and the OCP determination. In some experimental trials, the potentiostat gave signal for tension overloads before an extrapolation from the Tafel region was possible. Under these circumstances, the experimental corrosion rate were not determined. Figures 6 shows examples of experimental polarization curves obtained with AlMg3.

From data reported in Table 4, interesting observations can be drawn.

When in contact with as-received M15, i.e. Fuel 2, the aluminium alloy AlMg3 shows the most active state, exhibiting lowest corrosion potentials. On the contrary, AISI 304 steel is clearly working in the passive region, as evidenced by the most electropositive corrosion potentials here measured.

The addition of water, even containing acidic contaminants, leads in all metals an increase of the working potential. For metals which do not easily exhibit active-passive behaviour, e.g., St52 and 100Cr6 carbon steels, this occurrence would reflect increasing corrosion rates. On the contrary, for active-passive metals, such like AISI 304 and AlMg3, increasing working potentials could also be beneficial, since the passive state can be more easily reached and maintained. Nevertheless, the potential correspondent to the active-passive transition normally increases in value as the amount of acidic contaminants (mainly [Cl⁻]) increases.

These results are consistent with the work carried out by P.L. De Anna [29]. He studied the effect of water and chloride ions on

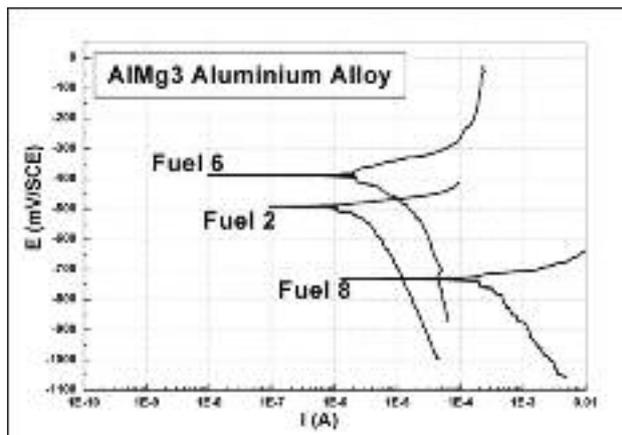


FIG. 6 Example of polarization curves of AIMg3 aluminium alloy performed in Fuel 2, 6 and 8.

Esempio delle curve di polarizzazione della lega AIMg3 nelle benzine 2, 6 e 8.

the electrochemical behaviour of iron and 304L stainless steel in de-oxygenated alcohols (methyl, ethyl, isopropyl, n-butyl and 2-chloroethyl alcohols). The author pointed out that the water concentration at the metal-solution interface differs from the bulk and that the solvent mixtures behave such that the less water-like alcohols (of lower dielectric constant) showing a stronger dependency on water concentration. By this way, the diffusion of water to the metal-solution interface is enhanced and therefore the passive film can result more stable. Moreover, chlorides exhibited a detrimental effect on corrosion in iron and 304L SS, particularly for concentrations above 10^{-3} M and 10^{-2} M, respectively.

Also the corrosion behaviour of carbon steels appeared dependent on the water content, acidity and amount of impurities of these ethanolic solutions. As the value of these variables increased, the corrosiveness of solutions reached values not compatible with the use of mild steels under both static and dynamic conditions, [30]. Nevertheless, the neutralisation of acidity with a shift of pH above 8 strongly decreased their corrosive potential, [30].

Experimental results confirm that an increase of fuel conductivity (from $0.5 \mu\text{S}/\text{cm}$ to $500 \mu\text{S}/\text{cm}$) and a decrease of fuel pH (from 7.3 to 0.5), for Fuels 7 and 8, induce a dramatic increase of corrosion potential for gasoline-alcohol blends.

CONCLUSIONS

Some generalizations can be made as result of this study. Austenitic AISI 304 stainless steel appeared to be fully compatible with as-received and modified fuels in all conditions here tested. This alloy exhibited a fully and complete passive state in all environments. Martensitic AISI 440 C stainless steel was able to develop a passive state when in contact at 18°C with both as-received E22 and M15 fuels, even though a loss of corrosion resistance was observed when exposed at higher temperatures (50°C).

Aluminium alloys (AIMg3, 6056 Aluminium alloy) were the poorest performers in these fuels, exhibiting damages under the form of surface pitting. Water additions might favour the instauration of a passive state, but acidic impurities and higher testing temperatures play an adverse effect to this respect. The corrosion potentials of AIMg3 within M15 were the lowest in value among tested materials. In case of absence of a passive state, in injection fuel systems a further intensification of corrosion damage may arise as consequence of galvanic coupling of

aluminium parts to more noble materials, such as stainless steels or copper.

Carbon steels exhibited reasonable resistances in as-received E22 and M15 fuels at 18°C . Nevertheless, increasing the test temperature at 50°C and using small additions of aggressive water to fuels, the corrosion rate increases by an order of magnitude. The typical corrosion morphology of carbon steels is surface pitting.

From these results it can be concluded that some of metallic materials today used in the fuel distribution, storage and dispensing systems could suffer problems when exposed to alcohols, either neat or in blends. The potential corrosiveness of these motor fuels is strictly dependent on their quality, e.g., amount of dissolved water and soluble contaminants (salts, organic and inorganic acids, chloride ions etc.). In order to give answers in term of compatibility of materials in these environments, it would be essential to give and impose reasonable limits to these variables.

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Abstract

Compatibilità dei materiali metallici nelle benzine alcoliche E22 e M15

Parole Chiave: acciaio, alluminio e leghe, corrosione

Nel presente lavoro sono stati studiati i fattori che influenzano il potenziale a corrosivo delle benzine alcoliche E22 e M15 tramite test di corrosione elettrochimici e per immersione. In particolare, è stato valutato il comportamento a corrosione di due acciai al carbonio (St 52, 100Cr6), di due acciai inossidabili (AISI 304, AISI 440 C), e di due leghe di alluminio (AlMg3, 6056 alloy). I test per immersione sono stati eseguiti a 18 e 50°C nelle benzine tal quali e con addizioni di contaminanti, quali acidi inorganici, ioni cloruro, sali, e acqua. L'acciaio inossidabile austenitico AISI 304 si è dimostrato pienamente compatibile sia con le benzine tal quali, che aggressivate, in tutte le condizioni sperimentali, dimostrando perciò la capacità di passivarsi in modo stabile in tali ambienti. L'acciaio inossidabile martensitico AISI 440 riesce a sviluppare uno strato passivante omogeneo solo a 18°C, subendo invece attacchi corrosivi localizzati (pitting) a 50°C.

Le leghe di alluminio mostrano le minori resistenze a corrosione, subendo anche intensi attacchi localizzati alle più alte temperature. Gli acciai a carbonio esibiscono resistenze ragionevoli solo nelle benzine tal quali a 18°C, mentre nelle miscele aggressivate ed a 50 °C sono anch'essi soggetti ad attacchi localizzati.

Dalle prove elettrochimiche è risultato che la lega AlMg3 ha il comportamento più attivo tra i materiali testati e che l'acciaio AISI 304 lavora stabilmente in zona passiva. L'addizione d'acqua comporta, in generale, un aumento del potenziale di lavoro dei materiali metallici e tale effetto può essere positivo per materiali a comportamento attivo-passivo come l'AISI 304 e l'AlMg3.

Dall'insieme dei risultati ottenuti, il potenziale corrosivo di queste benzine appare essere strettamente dipendente dalla loro qualità, in termini di quantità d'acqua e quantità e tipo di contaminanti acidi e sali solubili. In particolar modo, la presenza di ioni depassivanti, quali i cloruri, incrementa in modo considerevole la conducibilità elettrica del film pseudo-acquoso formato sulle superfici metalliche e rende più problematica la formazione/stabilità di eventuali film di ossidi passivanti.