FTIR CARACTERIZATION OF ANODIC ALUMINIUM OXIDE PROTECTIVE FILMS PRODUCED BY ANODIZING IN TANNINS

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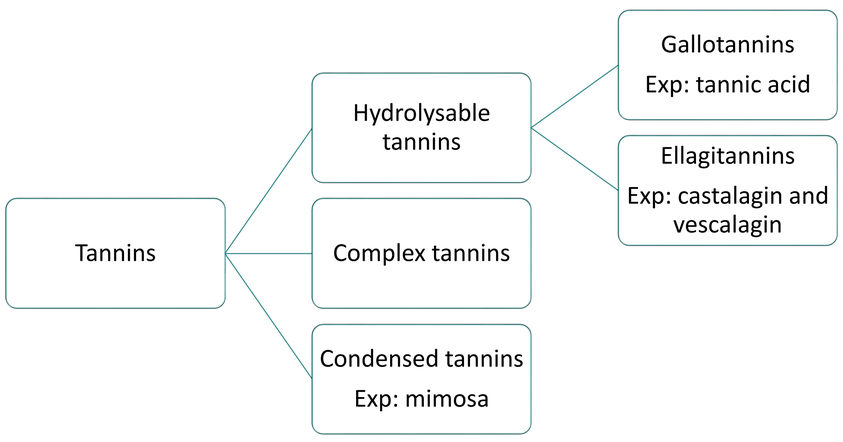
Introduction

The former conventional pre-treatment of AA2024-T3 aluminium alloy involves formulations containing chromium (VI) but REACH (Registration, Evolution, Authorization and Restriction of CHemicals) restricts the use of hexavalent chromium in EU, due to the negative impact of these compounds in environment and human health. In recent years there has been an increased interest in developing new corrosion protection alternatives, that could be efficient and more environmentally and human-friendly, to replace the chromium (VI) based treatments. Numerous alternatives have been described in the literature, composed of mixture of inorganic/organic acids. For example, the process licensed by Boeing uses a mixture of boric/sulphuric acid and the Airbus employs the tartaric/sulphuric acid (TSA).

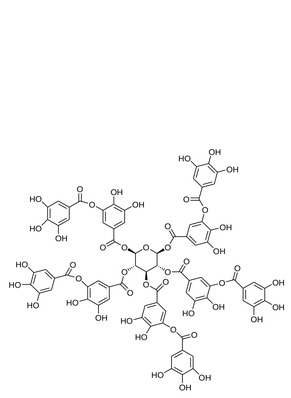
The conversion coatings formed on the aluminium alloy using several natural tannins obtained from renewable sources revealed that the use of these tannins, despite the differences in their chemical structures, provide a good corrosion protection, making this pre-treatment a promising alternative for chromium (VI) based chemical conversion In this work the Fourier Transform Infrared Spectroscopy (FTIR) spectra of anodizing and anodizing and sealed samples of AA2023-T3 was recorded and the shifts in the band position confirm that the green inhibitor interacts with the metal surface. FTIR data confirms that the films are formed by interation between of OH groups present in the tannins structure and the Al^{3+}.

Experimental

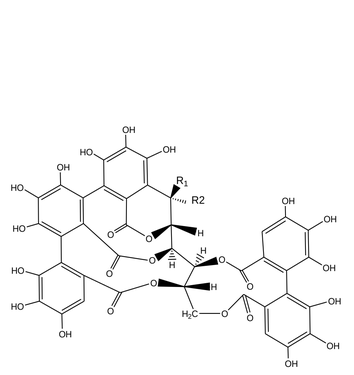
FTIR analyses were carried out using a Nicolet 6700 spectrometer (Thermo, Italy) equipped with a SAGA device. Spectra were recorded in the 4000-400 cm^{-1} range with a resolution of 4 cm^{-1}, averaging 128 scans per sample. Data was collected with Omnic 3.1 software.



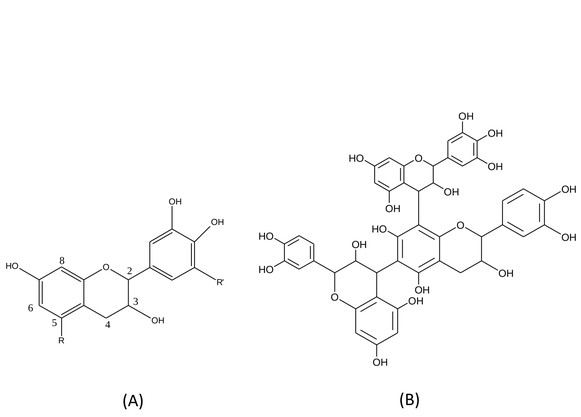
Chemical structure of gallic acid.



Chemical structure of tannic acid.



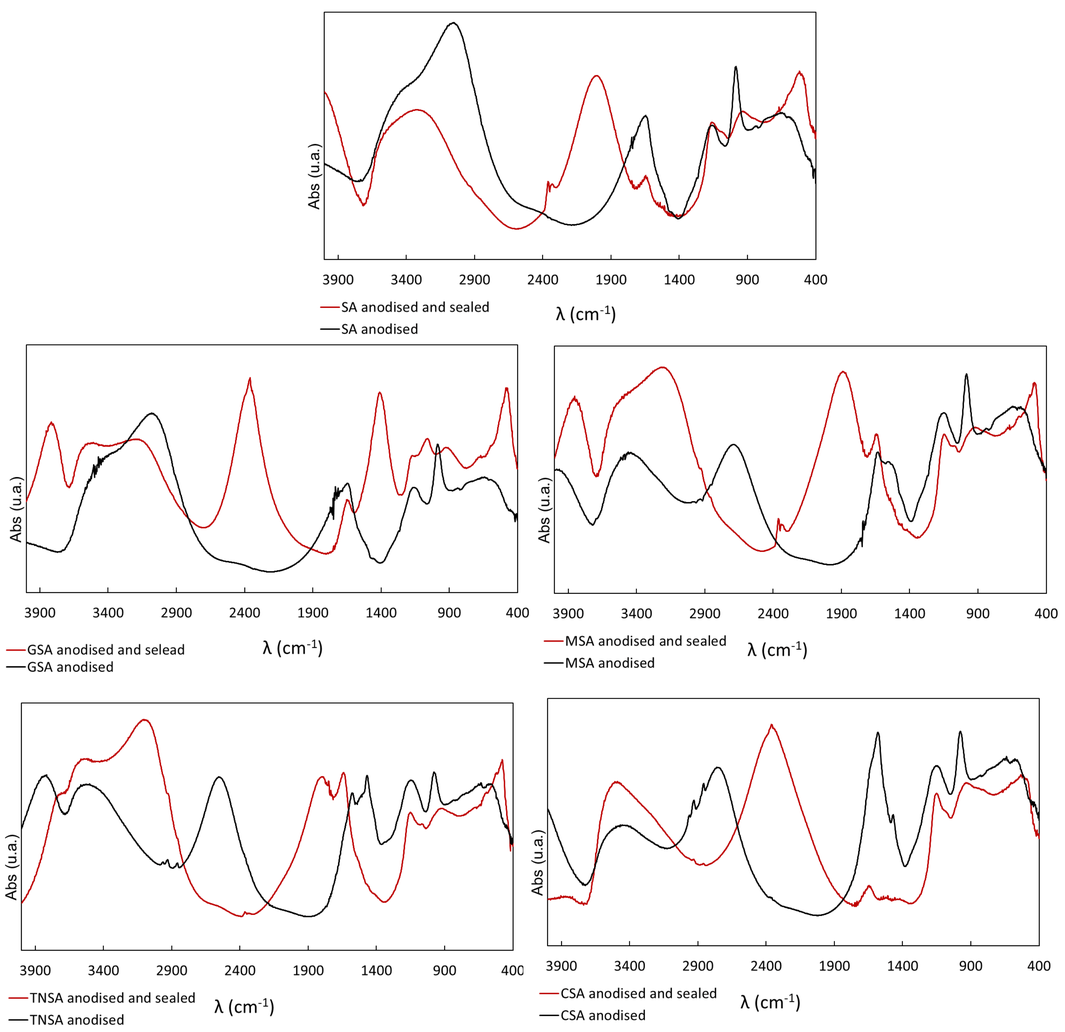
Chemical structure of castalagin (R_1=H, R_2=OH) and vescalagin (R_1=OH, R_2=H)



(A) (B)

Chemical structure of the main polyphenol unit of mimosa tannin (A) and the major trimer (B).

Results



FTIR absorption maxima observed in spectra of porous aluminium oxide produced in a 0.46M H_2SO_4 solution containing the green inhibitor.

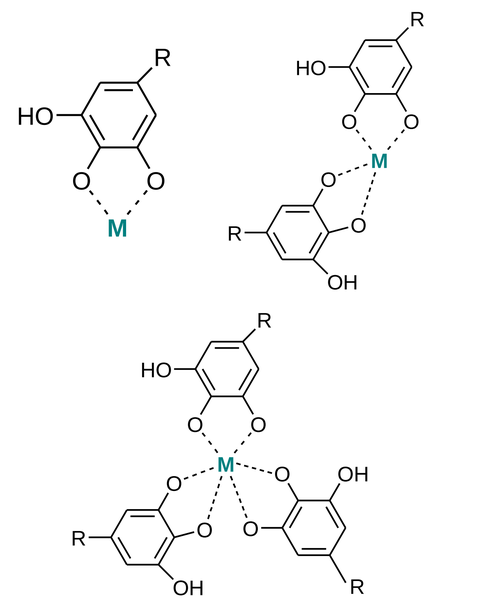
SA	GSA	TNSA	CSA	MSA	Assignments
		3815vs	3990vs	3963vs	ν_{as} O-H
3414vs	3400vs	3531vs	3446vs	3427vs	νO-H streching
3037vs	3062vs				
1635vs	1637m			1624s	νO-H (H_2O) and ν_sCOO-
		1552s	1577s	1543s	ν_{as}COO-
		1464s	1475s		
	1142m	1132m	1132s	1134m	ν C-O-C cyclic ether
980s	980s	980s	980s	980s	ν_{as} AlO_4 and δAlO_4
629vw	633vw	638w	629w	623w	ν_{as} AlO_4
561s	560w	559w	561w	530w	ν_{as} AlO_6

FTIR absorption maxima observed in spectra of porous aluminium oxide produced in a 0.46M H_2SO_4 solution containing the green inhibitor after the sealing process.

SA	GSA	TNSA	CSA	MSA	Assignments
3984VS	3813vs		3826vs	3840vs	ν_{as} O-H
		3695vs			ν_s O-H
3325vs	3495vs	3537vs	3485vs	3477vs	νO-H streching
	3174vs	3089vs		3190vs	
1635w	1635m	1635s	1633w	1641m	νO-H (H_2O) and ν_sCOO-
1151m	1155m	1144m	1140m	1138m	ν C-O-C cyclic ether
	1051w	1059vw	1078vw	1057w	β=C-H deformation
947w	903w	908w	918w	916w	ν_{as} AlO_4 and δAlO_4
654vw	650vw			665w	ν_{as} AlO_4
501s		513vw	511w	519w	ν_{as} AlO_6
	476s	476s	478w	476s	δAlO_4

vs: very strong; s: strong; m: medium; w: weak; vw: very weak.

The presence of ν_{as}COO- bands and the shift of νO-H streching in **FTIR** spectra allows to conclude that tannins interact with the metal probably by coordination:



Structure for the mono-complex, bis-complex and metallic tannate chelate where R represents the rest of the tannin molecule.

Conclusions

The use of FTIR analysis showed that tannins were absorbed on the surface of the metal thereby protecting it from further corrosion attack. FTIR spectra confirm the complexing of tannins with metal ions and allows to conclude that the interaction between the metal and the inhibitors occurs by OH and COO groups present in the inhibitors.

Acknowledgements

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