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Characterization of Solid Residues Emerging During Ultrasonic Cleaning Treatments of Tyre Moulds

The present paper aims at the investigation of the nature and possible origin of solid residues found in the washing basins of Ultrasonic Mould Cleaning System (UMCS) plants. In particular, analyses have been focused on the potential PTFE provenience of the debris and the eventual effect of acid solutions used in the process. Moreover, spring vents taken apart from tyre moulds subjected to repeated use and cleaning cycles, have been analysed in order to determine signs of wear, damage extent and its possible causes. Analyses have been performed by means of FT-IR, TGA, SEM-EDX and XRF, obtaining information on both organic and inorganic fractions. Results obtained seem to indicate that the degradation of PTFE is not responsible of the presence of these debris, and the acid solutions used in the process appear not to have a significant or direct role in the degradation and oxidation patterns.

Keywords: Tyre moulds, Ultrasonic cleaning process, Analysis of solid residues, TGA, FT-IR, SEM-EDX, PTFE, spring vents

1. INTRODUCTION

The present experimental study is a natural complement to previous works by authors aimed at the investigation of the surface modification of Teflon gaskets subjected to a combination of acid attack and temperature for long periods of time. In this work, residues found in washing basins of real plants designed for tyre moulds cleaning have been subjected to analysis in order to determine their nature and to individuate their provenience. These fragments are in form of black solid material, with different degree of agglomeration, from powder to larger particles (up to 5 mm). Moreover, some of the spring vents from tyre moulds subjected to cleaning operations have been removed in order to analyse them. In fact, these vents show areas covered by what seems to be a thin layer of different colour. These two unexpected signs of possible degradation phenomena have been subjected to more in-depth studies.

Mould cleaning and maintenance are of major concern for the tyre industry. The cleaning process of the moulds must remove fouling and residues of rubber from the inner surfaces, avoiding wear of the mould design itself (Figure 1). A number of technologies are available, each with specific advantages and drawbacks. A comparative assessment of tyre mould cleaning solutions is presented in [1]. It is reported that Ultrasonic Mould Cleaning Systems (UMCS) represents a better choice in case of complex and fragile geometries (e.g. spring-vents). The UMCS technology is a multi-step process that sees the concurrent use of ultrasonic waves, moderate temperature and acid solutions, that is used to remove rubber scraps and other

debris from recess of the moulds.

Tyre moulds and their parts are immersed in a sequence of washing baths, where the residues are attacked and the mould surfaces cleaned.



Figure 1: Detail of a spring vent extracted from a tyre mould subjected to analysis

While these environmental conditions permit to efficiently clean the moulds, several parts of the plants (as metal sheets, welds and flange Teflon gaskets) are exposed to the same deteriorating phenomena. Their progressive degradation under the persistency of all these operative conditions, including a correct recognition of mechanisms of wearing (e.g. fatigue, fretting, corrosion, aging etc.), represents a relevant field of investigation with the aim to optimize the process.

Recently, minor several failures, as the loss of drops of cleaning solution from washing basins in a UMCS plant, highlighted an unexpected seal deterioration. In particular, Teflon tapes used as gaskets in the acid basins exhibits degradation, especially on the surface, incompatible with normal conditions of use [2]. In fact, according to the state-of-art and technical datasheet,

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Teflon, brand name for Polytetrafluoroethylene (PTFE), reveals a great thermal and chemical stability that make this material a valid choice in a large number of practical applications [3, 4]. In the operative conditions characterizing the UMCS plants (as Temperature, pH), no relevant degradation in PTFE was expected [5, 6]. However, evidences from operation [7] suggested that one or more unexpected phenomena occurred. In fact, referring to [8-10], it is stated that only under very uncommon circumstances PTFE degrades. In particular, the carbon-fluorine bonds in the PTFE can be effected by alkali metals (i.e. zinc oxide, present in 1-2 %wt. in the rubber as vulcanization activator [11]), and fluorinating agents.

In order to understand the reasons behind this uncommon behaviour, an intense research activity has been developed. A first comparative analysis was performed on PTFE gaskets before and after the use in UMCS by means of mechanical tests and micrographs [12]. Results showed a not negligible difference between the two situations. Afterwards, a more in-depth comparison between unused and aged in controlled environment (temperature, acids) PTFE gaskets was also conducted and results presented in [13-15].

In particular, [13] describes the aggravated conditions of heat and acid attack (with an almost pH 1 solution composed by a mixture of sulfamic, hydrochloric and hydrofluoric acids, and, simultaneously, a temperature between 70 and 80°C) used to speed up the normal aging processes of PTFE gaskets, in the way to correctly represent their utilisation inside the UMCS plants. Besides, [14, 15] describe the effects of aging on PTFE chemical surfaces by Fourier Transform Infrared Spectroscopy (FT-IR) and exhaustive thermal analysis (TGA and DSC), permitting preliminary considerations regarding the use of PTFE in UMCS conditions and its aging mechanisms.

The present research describes the spectroscopic, thermal and elemental analysis performed on the solid residues found in the washing basins, and on spring vents taken apart from tyre moulds. These analyses are aimed to the identification of the possible provenience of the debris and the causes of the damages detected on the spring vents. In particular, it has been considered of crucial importance to confirm or exclude the possible provenience of these residues from the PTFE gaskets previously analysed.

2. MATERIALS AND METHODS

Samples have been at first visually inspected by means of a Zeiss Axio Vert Imager.A1m microscope and a Hirox 3D Multifocal Microscope model HX 7700 in order to investigate the surface of the particles. Samples have been observed at different magnification, ranging from 2,5x to 100x.

The different morphologies individuated have been then subjected to μ FT-IR analysis, by means of a Perkin Elmer Spotlight 200 FT-IR microscope, coupled to a Perkin Elmer Frontier optical bench. Spectra have been acquired in μ ATR mode equipped with a germanium crystal, in the 4000-650 cm^{-1} range with a spectral

resolution set to 2 cm^{-1} and 64 scans per spectra in order to lower signal-to-noise ratio (SNR). Coarser particles have been subjected to ATR analysis by means of a Perkin Elmer Frontier equipped with the UATR module, in the 4000-650 cm^{-1} range, spectral resolution set to 4 cm^{-1} and 4 scans per spectra.

Electronic Scanning Microscopy coupled Energy Dispersion X-Ray Spectroscopy (SEM-EDX) have been performed on both the residues and some spring vents coming from the two parts, lower and upper, of a tyre mould. The analyses have been performed by means of a Scanning Electron Microscope (SEM) ZEISS EVO 50 EP in Environmental mode with \approx 100 Pa pressure in the chamber.

Changes in physical and chemical properties of the residues materials have been measured by TGA as a function of increasing temperature [16-18]. In particular, in the present work, TGA has allowed the characterization of materials through the analysis of characteristic decomposition patterns and the evaluation of degradation mechanisms and reaction kinetics. By TGA, it has been also possible to verify the presence (or absence) of organic/inorganic contents. The two main different morphologies individuated have been then subjected to thermogravimetric analysis (TGA), by means of a TA Q600 instrument, set to a heating rate of 10 $^{\circ}\text{C}/\text{min}$, from room temperature to 750 $^{\circ}\text{C}$. TGA analyses have been performed on 6-8 mg of material and in inert atmosphere (N_2 , 100 mL/min) until reaching 750 $^{\circ}\text{C}$, then the atmosphere has been switched to air in order to oxidize any eventual organic residue [19]. Evolved gases has been continuously transferred to an Agilent Cary 660 FT-IR optical bench through a transfer line kept at 280 $^{\circ}\text{C}$ to avoid any condensation of the substance present in the gases. FT-IR Spectra of the evolved gases have been acquired every 4 seconds, in the 3800-650 cm^{-1} range, with a spectral resolution of 4 cm^{-1} [20].

X-ray Fluorescence spectra have been acquired by means of a PANalytical AxiosMAX Advanced XRF Spectrometer, equipped with a rhodium X-ray tube target, set to a power of 2.4 kW in order to identify the possible presence of chlorine, fluorine or other elements. These analyses were taken as a confirmation of the EDS spectra. In fact, while the latter is a punctual analysis, the former is a bulk analysis and should eliminate possible anomalous results and spot identifications.

3. RESULTS

The visual inspection, performed with both Zeiss confocal microscope and Spotlight 200, of the different samples of solid residues shows two different morphologies, named A and B, as can be seen by the series of images reported in Figure 2 for the sample A and Figure 3 for the sample B.

The two different morphologies have been recognized due to difference of the surfaces, in terms of colour and aspects: rough, uneven, less thick and dark coloured the first (A); more smooth, plain, compact and light coloured the latter (B). In order to determine eventual compositional differences between the two

morphologies identified, FT-IR in ATR/ μ ATR mode, thermal and elemental analysis have been performed on the two samples.

In Figure 4 are reported the FT-IR spectra (ATR and μ ATR) of the samples A and B.

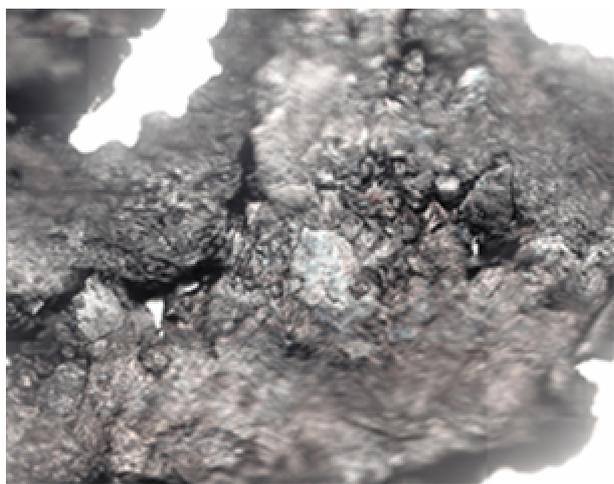
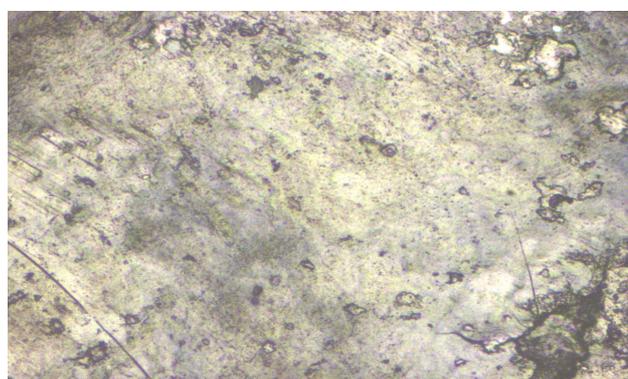
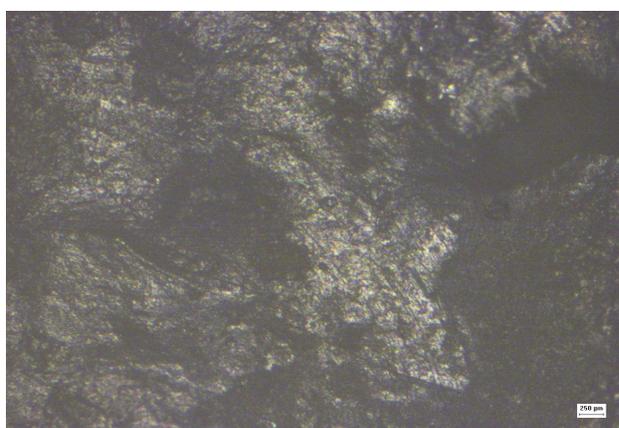
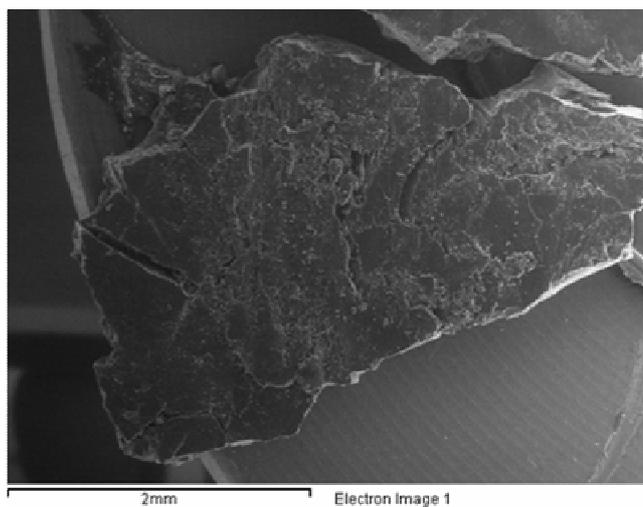
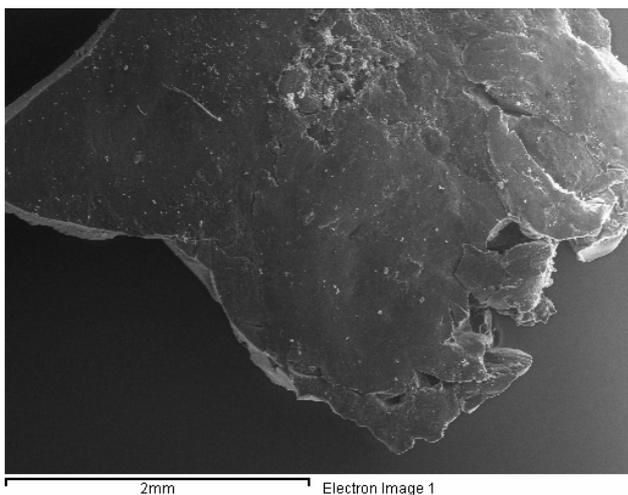


Figure 2: Different micrographs of particles named A with rough, uneven and darker surfaces. SEM (top), confocal microscope (centre) and Spotlight 200 FT-IR microscope (bottom)

Figure 3: Different micrographs of particles named B with more even, brighter and glass-like surfaces. SEM (top), confocal microscope (centre) and Spotlight 200 FT-IR microscope (bottom)

The comparison of the spectra reported in Figure 4 seems to indicate that the chemical nature of the two morphologies identified from visual inspection could be considered almost identical. In fact, both samples show major signals at 2849, 2917 and 2956 cm^{-1} . These

signals are attributable to C-H stretching absorption typical of extended aliphatic chains with unsaturated bonds, which may be ascribed to fragments of polymers like polyisoprene or polybutadiene. However, a slight difference can be seen between the two samples.

Spectra of B samples show signals at 1701 and 1710 cm^{-1} , that are possibly attributable to carbonyl (C=O) groups. These signals may be considered as signs of slightly higher degradation by oxidation of B samples, compared to A ones [21-23]. The complete absence of signals at about 1200 and 1148 cm^{-1} , which are related to symmetric and asymmetric stretching vibrations of CF_2 bonds [24-26], seems to exclude the presence of PTFE residue and, therefore, the Teflon provenience of these debris. This was one of the possible sources due to gaskets failure used in the same plants, as already investigated [14, 15]. Figure 5 shows the superposition of the FT-IR spectra of sample A, B and of the PTFE gaskets as well as reported in [14].

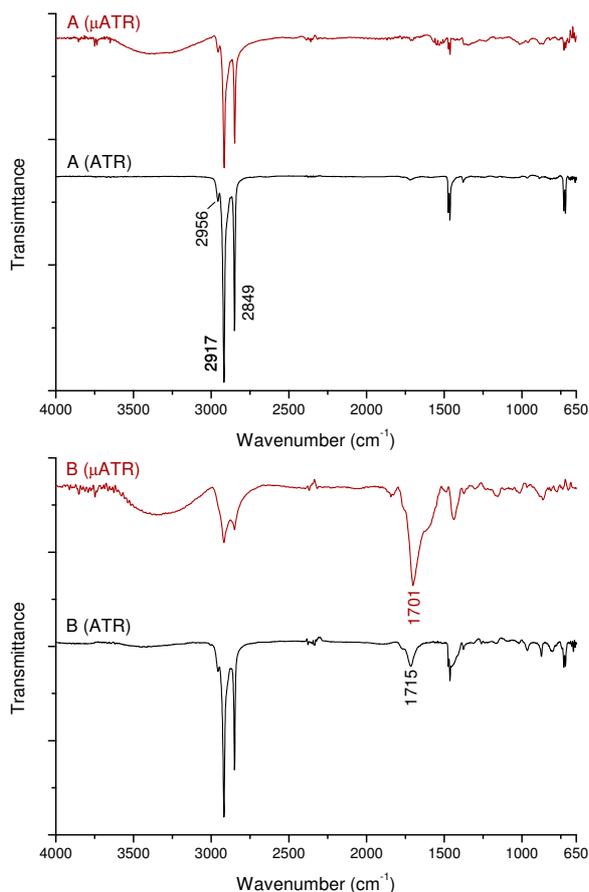


Figure 4: ATR/ μ ATR spectra of the two samples of solid residue (A, top; B, bottom)

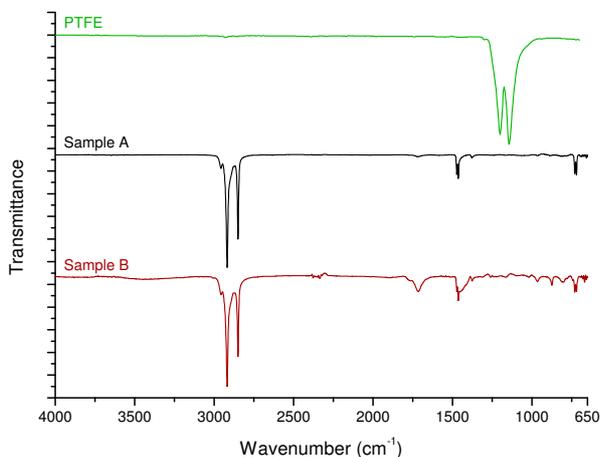


Figure 5: FT-IR-ATR spectra of the two different morphologies (A and B) compared to a new, unused PTFE gasket

Samples A and B have been then subjected to thermogravimetric analysis (TGA), in order to characterize their thermal properties. Thermograms are reported in Figure 6, and results are summarized in Table 1.

From the point of view of thermal properties, it can be seen that the two sample behave in an almost identical manner. The initial minor weight losses occurring for both samples at about 100 – 110 $^{\circ}\text{C}$ were not taken into account because they have been considered to be simple humidity retained by the samples. Major differences may be found in the entity of the first weight loss (1 in Table 1), which is slightly greater and occurring at few Celsius degrees higher for sample B. This fact could possibly mean that the organic (i.e. polymeric) fraction is higher compared to Sample A.

The second weight loss (2 in Table 1) correspond to the complete oxidation of the samples, after the atmosphere switch from nitrogen to air. These losses show an opposite behaviour, with slightly higher entity of the weight loss and peak temperature for sample A, possibly suggesting a higher carbon-to-oxygen ratio compared to sample B. Moreover, sample A residue is higher than that of sample B.

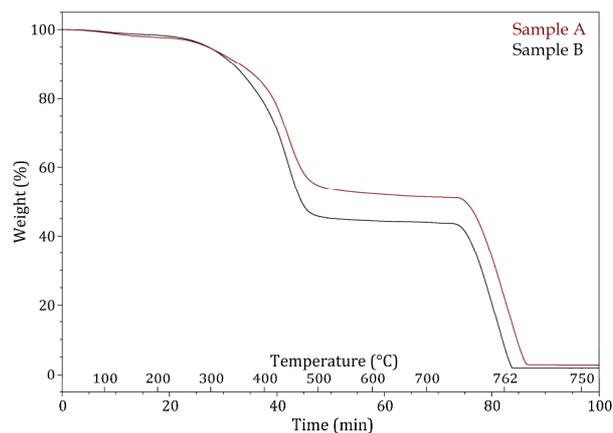


Figure 6: TGA thermograms of sample A (red) and B (black)

Table 1: TGA relevant results of Sample A and B

		A	B
1	T_{peak} ($^{\circ}\text{C}$)	437	443
	t (min)	42.1	42.0
	Weight loss (%)	45.3	53.4
2	T_{peak} ($^{\circ}\text{C}$)	762	761
	t (min)	83.3	80.6
	Weight loss (%)	49.6	42.5
Residue (%wt)		2.80	1.93

With the intention of carry out a more in depth analysis, the evolved gases arising from the TGA have been continuously sampled and analysed by FT-IR. The resultant spectra are reported in Figure 7.

It can be easily seen that the two spectra almost perfectly overlap, which may suggest that the organic component of the two samples should be the same. The comparison performed using the spectral libraries available suggest that the gases could be composed of octene or decene (aliphatic chain) as well as reported in Figure 8.

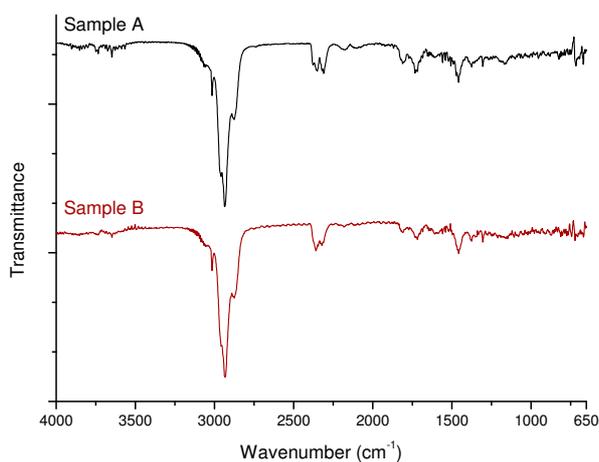


Figure 7: FT-IR spectra of the evolved gases from TGA. Sample A (top) and Sample B (bottom)

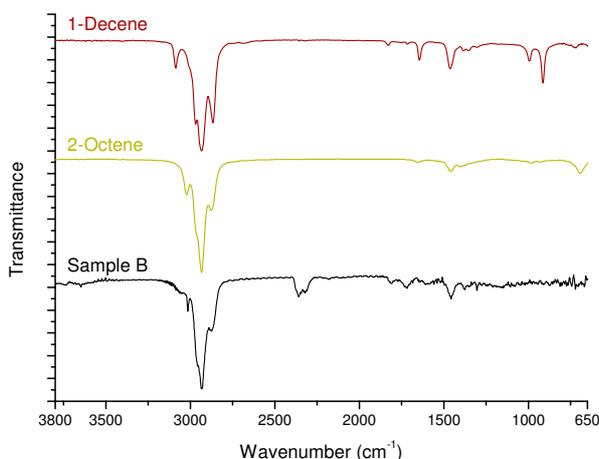


Figure 8: spectral libraries comparison between FT-IR spectra of evolved gases from B with 2-Octene/1-Decene

This result seems to indicate the presence of relatively short aliphatic fragments with unsaturated bonds, due to the thermal fragmentation of longer polyene chains, in accordance to what emerged from the ATR/ μ ATR analysis of both samples.

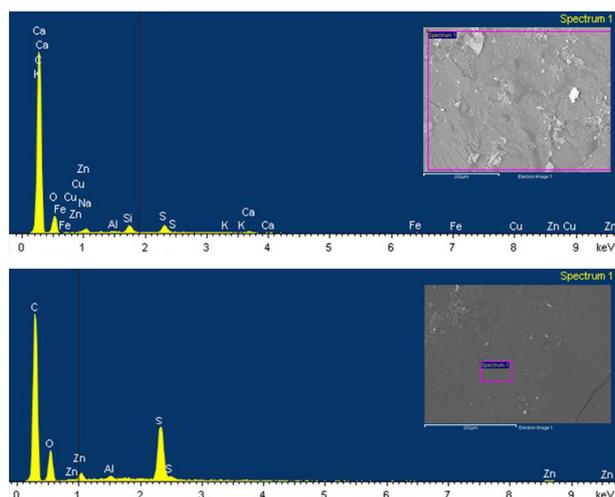


Figure 9: SEM micrographs and related EDX spectra of sample A and Sample B

Finally, elemental analysis by means of SEM-EDX, has been done in order to determine the elemental composition of the two samples and to investigate also the inorganic composition of the debris. Different

specimens for each of the two samples A and B have been analysed and for each specimen various sampling points have been chosen, in order to minimize spot errors and have the most faithful elemental composition. Moreover, large sampling areas have been subjected to scanning and automatic averaging of the data, in order to have a mean composition of the specimens, as reported in Figure 9.

The elemental composition, by EDX analysis, of both samples is reported in Table 2.

Table 2: EDX analysis of representative specimens belonging to Sample A and Sample B

	Sample A	Sample B
	%wt	
C	78.5	69.3
O	17.6	23.6
Na	0.3	-
Al	0.1	0.2
Si	0.7	-
S	0.9	5.4
K	0.1	-
Ca	0.3	-
Fe	0.3	-
Cu	0.5	-
Zn	0.8	1.5
Total	100.0	100.0

The elemental composition of both samples show the presence of carbon and oxygen as the two major elements. The latter is present at higher weight percentage in sample B, in accordance with FT-IR analysis, and could allow to confirm that sample B is more oxidized than sample A. Further analysing the data allow to notice the presence of quite high quantity of sulphur and zinc. These two elements are typically present in tyre rubber formulation as vulcanization agent and accelerator, respectively [11]. However, the quantity of these elements is relevantly higher in sample B: sulphur quantity is six time higher, while zinc is the double. On the other hand, sample A is composed also by small quantities of alkali and alkaline earth metals (sodium, potassium, calcium), metalloid (silicon) and transition metals (iron and copper). While some of these elements are commonly found in tyres pyrolysis char, the percentages found in the investigated samples are significantly higher [11].

Furthermore, EDX spectra of other peculiar spots of the solid residue samples have been acquired. These spots appear like micrometric particles adhering on the surface, as show in Figure 10, where the most relevant EDX spectra and corresponding micrographs of the acquired sample area are reported.

The chemical composition of these micrometric grains is reported in Table 3. It results that the most abundant elements are transition metals. In fact, a part from carbon and oxygen, both still present but clearly decreased in quantity, other major elements identified are copper and tin, with the simultaneous presence of zinc in one case (B1).

Only A2 sample contains iron. Sulphur is still present, but in a significant reduced extent when compared to A and B samples (see Table 2). However, the presence of sulphur maintains the same trend seen

before, with A1 and A2 samples exhibiting less quantities than B1 and B2 samples.

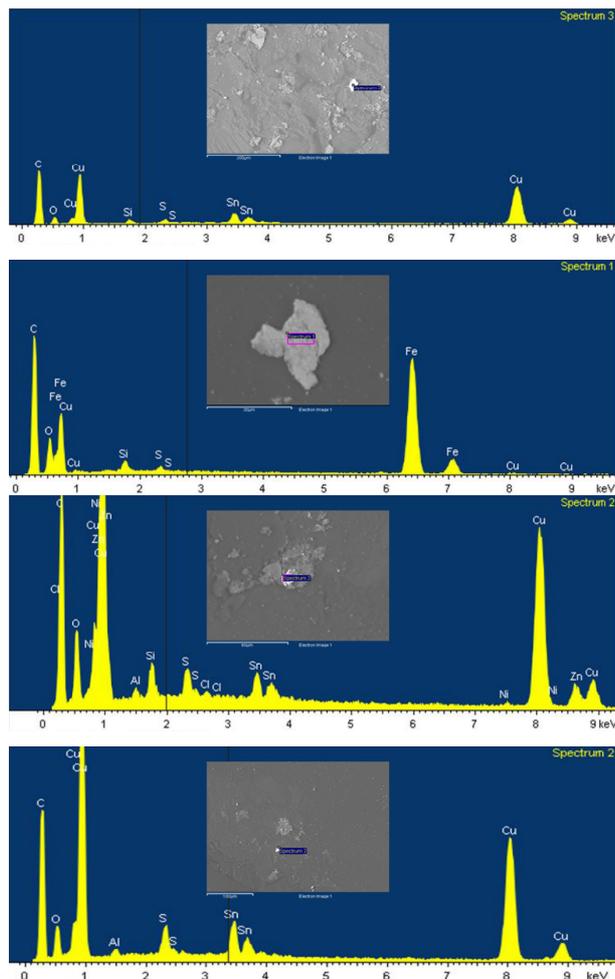


Figure 10: SEM micrographs and related EDX spectra of peculiar spots over the surfaces of sample A and Sample B. Top to bottom: A1, A2, B1, B2

Table 3: EDX analysis of the peculiar spots belonging to Sample A and Sample B.

	A1	A2	B1	B2
	%wt			
C	47.2	49.0	43.0	43.6
O	6.3	13.5	10.4	8.2
Al	-	-	0.3	0.4
Si	0.7	0.7	1.0	-
S	0.5	0.3	0.8	1.4
Cl	-	-	0.2	-
Ni	-	-	0.4	-
Fe	-	36.0	-	-
Cu	39.9	0.5	36.3	40.6
Zn	-	-	4.9	-
Sn	5.4	-	2.7	5.8
Total	100.0	100.0	100.0	100.0

The two samples have been finally subjected to XRF analysis with the aim to confirm the elemental composition determined by EDX. Moreover, the former is a bulk analysis and results may be considered as representative of the whole material, and not only of the

surface like the latter. The main results are reported in Table 4.

Table 4: XRF analysis of the two samples

	Sample A		Sample B	
	%wt			
	As is	Normalized	As is	Normalized
Na	0.08	1.4	0.19	3.1
Mg	0.05	0.9	-	-
Al	0.13	2.3	0.09	2.0
Si	0.21	3.7	0.21	3.9
P	0.03	0.5	-	-
S	0.84	14.4	0.89	18.9
Cl	0.24	4.2	0.18	4.4
K	0.09	1.5	-	-
Ca	0.22	3.8	0.14	4.0
Cr	0.09	1.6	0.08	1.8
Fe	0.17	3.0	0.06	1.3
Cu	0.08	1.5	-	-
Zn	3.56	61.4	2.85	60.6
Total	5.80	100.0	4.70	100.0

Results are expressed as weight percentages, as is and normalized. Pre-normalization weight percentages of the samples were 5,80 % (Sample A) and 4,70 % (Sample B), meaning that Sample A has a higher inorganic content and compositional variety, in accordance also with TGA and EDX results. The most abundant elements presents are zinc and sulphur, with the latter slightly more abundant in Sample B, confirming the trend highlighted by EDX results. However, both zinc and sulphur seem to be present in quite more similar quantities than resulted from EDX analysis, strongly suggesting the same provenience of the solid residues. The differences between bulk (XRF) and surface (EDX) analysis could possibly mean a greater surface compositional variability than expected. It could not be excluded the possibility of a contribution of sulfamic acid, although FT-IR spectra has not revealed bonds containing sulphur. Fluorine is completely absent and the minimal percentages of chlorine are consistent with EDX results.

At last, SEM-EDX analysis has been performed on some spring vents from the tyre moulds actually subjected to different cleaning cycles in the UMSC plants. Figure 11 shows a micrograph of the whole spring vent subjected to analysis. It can be seen that the surface is evidently damaged, with a consistent part covered by a dark coloured layer, and the diffused presence of reddish stains normally associated with iron oxides.



Figure 11: Hirox 7700 micrograph of the spring vent

Figure 12 shows SEM micrographs of the more interesting sampling areas examined. Some parts of the spring vent are covered by a thin black layer (I-II), while other parts appear less damaged (III), or nearly intact (IV).

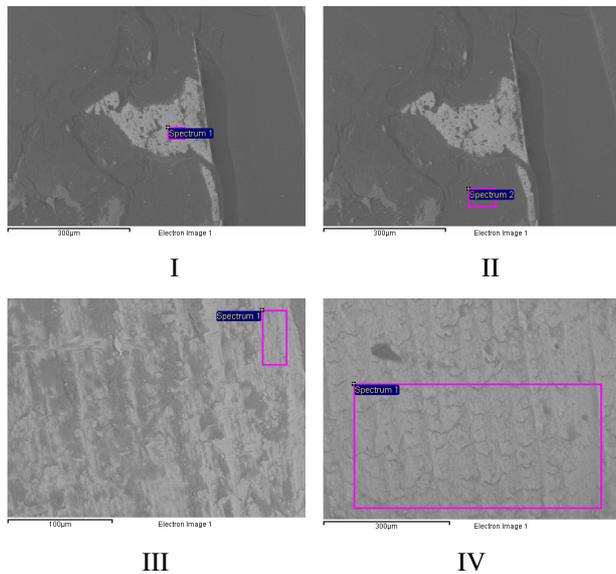


Figure 12: SEM micrographs and sampling area of the surface of a tyre mould spring vent

The elemental analysis corresponding to the micrographs of Figure 12 are reported in Table 5.

Table 5: EDX analysis of the different sampled areas of spring vents.

	I	II	III	IV
	<i>%wt</i>			
C	31.8	68.9	9.1	13,0
O	11.6	25.4	16.8	24,8
Na	-	-	-	-
Mg	-	-	1.5	-
Al	-	-	9.1	1,0
Si	-	-	0.4	0,4
S	1.3	2.0	1.0	0,8
K	-	-	-	0,3
Cr	-	-	0.3	0,3
Mn	0.5	-	1.4	1,5
Fe	54.0	2.5	60.6	58,0
Zn	0.8	1.3	-	-
Total	100.0	100.0	100.0	100,0

It seems reasonable that the black thin layer analysed in II could be related to the composition of the debris found at the bottom of the basins, thus to the possible tyre rubber composition (Table 2). In fact, it is possible to observe, besides carbon and oxygen, the presence of moderate quantities of sulphur and zinc. The metallic spot in the same frame, analysed in I still shows the presence of carbon, but the most abundant element is iron. The same is for III and IV, which show, in addition, relevant quantities of aluminium and manganese, as well as low content of silicon and chrome. These former elements are not typically found in tyre rubber compounds and are plausibly arising from treatments carried on the spring vents.

4. CONCLUSIONS

The present paper describes an in-depth characterization of solid residues emerged from washing basins in Ultrasonic Mould Cleaning System (UMCS) plants. Also, spring vents coming from repeatedly used and treated tyre moulds have been examined and subjected to analysis. The aim was to determine the origin of these signs of wear, and to verify the possible contribution of the acid solutions used in the washing basins. Moreover, having previously observed failures of Teflon gaskets used in these basins, the analyses was also aimed to confirm or exclude the possible PTFE nature of the debris and, thus, major and dramatic Teflon gaskets failures.

Fourier-Transform Infrared spectroscopy (FT-IR), thermal analysis and evolved gases analysis (TGA/FT-IR), energy dispersive X-ray spectroscopy (EDX), consequent to SEM analysis and finally X-ray fluorescence (XRF) spectroscopy have been performed on two solid residue samples with different morphologies previously identified by visual inspection by means of different type of microscopy.

The results obtained seems to indicate that the debris could be modified (i.e. oxidized) residues of tyre rubber arising from the moulds. Neither the FT-IR spectra nor the elemental analyses (EDX, XRF) show any trace of fluorine or carbon-fluorine bonds, therefore the PTFE gaskets are not responsible for these debris.

The different morphologies of the solid residues identified are slightly different in composition, with one of the two (B) showing slightly major oxidation according to FT-IR and EDX analysis. The other sample (A) exhibits minor quantities of alkali and alkaline earth metals (magnesium, potassium, calcium) and transition metals (iron and copper). The presence of these elements, and the related ashes, could be the reason of the faintly higher residue at 750 °C according to TGA results. FT-IR spectra acquired on the surface of the debris has not highlighted functional groups containing sulphur.

Both samples show substantial concentrations of vulcanization agents like sulphur and zinc, as confirmed by EDX and specially by XRF analyses. Finally, the analysis of spring vents taken from a tyre mould cleaned in the UMCS plant revealed the presence of thin layers of carbonaceous material, with composition similar to that of the debris, thus attributable to the tyre rubber compound, and also spots of typical iron oxidation.

In conclusion, the analyses performed on the residues exclude the PTFE origin of these debris. Moreover, both solid residues and spring vents show wear signs that are not directly attributable to the acid mixes used in the washing cycles of the UMCS plants. In fact, chlorine, fluorine and residues of sulfamic acid were not unarguably detected in any of the samples by any of techniques employed.

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**КАРАКТЕРИЗАЦИЈА ЧВРСТОГ ОСТАКА
НАСТАЈА ТОКОМ УЛТРАЗВУЧНОГ
ТРЕТМАНА ЧИШЋЕЊА КАЛУПА ГУМА**

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Овај рад има за циљ истраживање природе и могућег порекла чврстих остатака нађених у постројењима са базенима за прање у ултразвучним системима за чишћење (UMCS). Конкретно, анализе су фокусиране на порекло потенцијалних PTFE остатака и евентуалног дејства киселих раствора који се користе у процесу. Осим тога, вентили узети из калуца гума подвргнути вишеструкој употреби и циклусима чишћења, анализирани су како би се утврдили знакови хабања, обими оштећења и могућности њихових узрока. Анализе су извршене помоћу FT-IR, TGA, SEM-EDXS и KSRF, добијањем информација како за органске тако и за

неорганске фракције. Добијени резултати указују да деградација ПТФЕ није одговорна за присуство ових остатака, и кисела солација коришћена у процесу

изгледа да немају значајну или директну улогу у деградацији и оксидацији.