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Flexible Sealants – An Analysis

ABSTRACT:

An encounter with flexible sealants during casework led to the purchase and analysis of three different brands of the aerosolized sprays.

KEYWORDS: Flexible Sealants, IR, SEM, Py-GC-MS, PLM

INTRODUCTION

Recently, a case was examined that involved footwear impressions in what was described as "Flex Seal paint" a product typically sold through TV advertisements. The ads indicate that it is an aerosolized spray that can be used to fill any cracks, seals, or other areas of damage around the house. After searches at various retail stores, three different brands of this type of "paint" were acquired: PMI Technology's Flex Seal®, Rust-Oleum's® LeakSeal™, and Home Armor's™ Flexible Sealer (Figure 1). The Safety Data Sheets for these products show that they all contain large amounts of hydrocarbons along with other extenders and compounds in varying amounts such as calcium carbonate, barium sulfate, and hydrogen sulfide.[1,2,3] The following is an analysis of these three different sealant products.

PROCEDURE

Each of the three brands was sprayed onto individual microscope slides and allowed to dry. Material from each slide was sampled with a scalpel and placed onto two additional slides. On one of the slides the sample was smeared to form a thin film and on the other slide the sample was dissolved in xylenes in order to separate the extenders from the binder for microscopy. Both slides were then observed with a Polarized Light Microscope (PLM, Olympus BH, mounting medium MeltMount™ refractive index 1.662).

The flexible sealants were further analyzed on a Fourier Transform Infrared Spectrometer (IR, two separately prepared samples for each compound , Nicolet Thermo Nexus 760, Diamond Anvil Cell), a Scanning Electron Microscope with Electron Dispersive X-Ray Spectroscopy attachment (SEM-EDX, Hitachi S-4000 (SEM), EDAX (EDX), multiple runs on one prepared sample focusing on specific particles), and Pyrolysis Gas Chromatograph Mass Spectrometer (Py-GC-MS, two separately prepared samples for each compound, CDS 5250 Pyroprobe (Py) (Method: 750°C for 15 seconds), Agilent

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7890A Gas Chromatograph (GC) (Split Ratio: 50:1, Column: 5% phenyl methyl siloxane, Method: 50°C for 1 minute, then 6°C/minute to 100°C, hold at 100°C for 1 minute, then 8°C/minute to 140°C, hold at 140°C for 1 minute, then 16°C/minute to 220°C, then hold at 220°C for 15.67 minutes), Agilent 5975C Mass Spectrometer (MS).

Figure 1 – The three brands analyzed

OBSERVATIONS

The texture of the dried sealants varied between the cans after spraying (Figure 2), but each appeared as a black coating (alternatively, some of the brands come in a white version as well). While spraying, it was noted that the sealants were emitted from the cans at differing amounts of force (nozzle design or other factors) which may account for the variance.

When sampled with a scalpel, the Flex Seal® and Flexible Sealer were both viscous. The LeakSeal™ sampled like a “typical” paint, peeling away. Both the Flex Seal® and the

Flexible Sealer smeared easily onto the microscope slides. The LeakSeal™ was more problematic and less prone to smearing, resulting in a thicker sample.

Figure 2 – Flex Seal®, LeakSeal™, and Flexible Sealer after drying.

PLM analysis of the smears showed opaque particles along with several dispersed birefringent particles of various sizes for each brand (Figure 3).

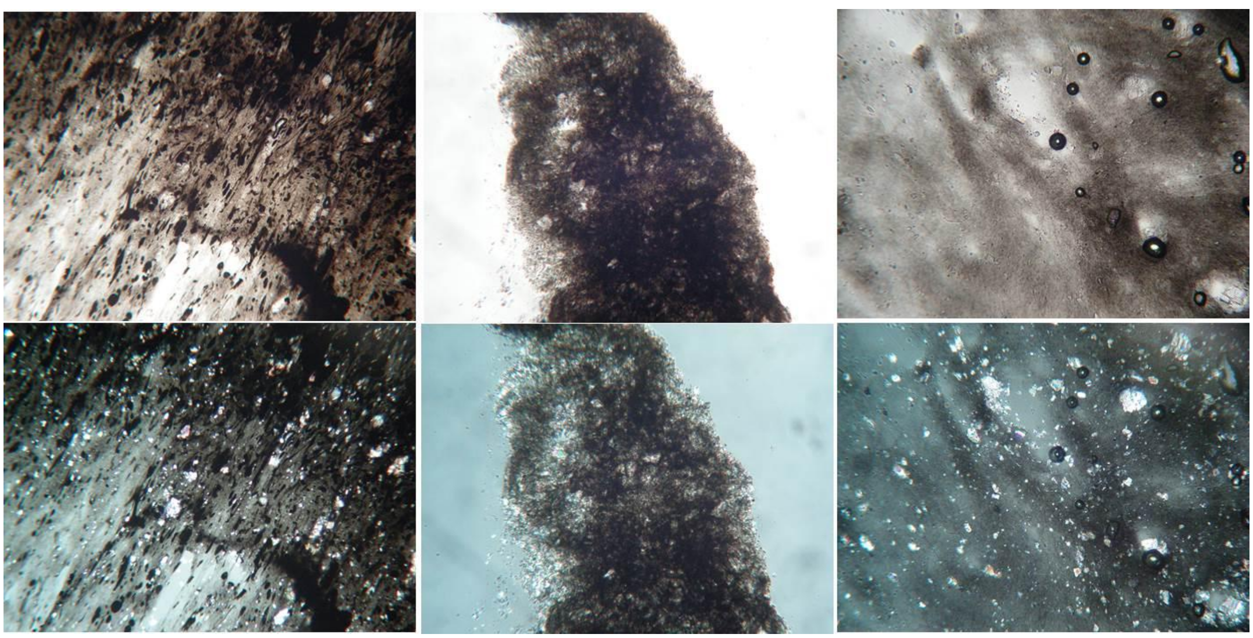

Figure 3 – Left to Right, PLM images of the smears of Flex Seal®, LeakSeal™, and Flexible Sealer. The top image is in polarized light; the bottom image is with slightly-uncrossed polars.

Calcite crystals of varying sizes were observed within the xylene dissolved samples (Figure 4). These were characterized by observing the striations on the crystal face and then noting that at one extinction value the crystal had high relief (in accordance with the n_ε of 1.48)[4] and at the other extinction had low relief (in accordance with the n_ω of 1.60)[5]. When viewed in high relief, the characteristic striations are observed in many of the crystals. Calcite was later confirmed with the IR.

Figure 4 – Calcite crystal example as seen in LeakSeal™ sample. Shown in high relief with characteristic striations.

IR spectra of the three brands showed similarities between the Flex Seal® and Flexible Sealer. The LeakSealTM had a noticeably different spectrum. All three brands had calcite bands (2515 cm^{-1}, 1797 cm^{-1}, 1424 cm^{-1}, 876 cm^{-1}) as well as styrene bands (a slightly shifted 760 cm^{-1} band as well as 700 cm^{-1}). The LeakSeal™ bands appeared to have a higher intensity of calcite than the other two. A rising baseline was observed in the spectra which was most likely due to carbon black (Figure 5).

Analysis with the SEM-EDX showed greater similarity in elemental composition between the Flex Seal® and the LeakSeal™ than with the Flexible Sealer, because of the detection of magnesium and aluminum (Figure 6). LeakSeal™ was shown to have a much higher prevalence of calcium. When an analysis was conducted focusing on specific particles, it was not possible to locate a particle in the LeakSeal™ that did not contain calcium. In contrast, particles without calcium were found in the in the Flex Seal® and Flexible Sealer. These are likely silicates. The element peaks for barium and sulfur were not observed in any of the samples which are in contrast to their being listed in at least one of the Safety Data Sheets.

Analysis with the Py-GC-MS showed similarities between all three brands due to the large styrene component and styrene pyrolysis byproducts that were observed (Figure 7). There were several differences in the ratios of the more intense peaks between the compounds but these were all determined to be styrene byproducts. From a comparison standpoint the only differences of note occur in the ratios of some of the more prevalent peaks, and in the data post twenty minutes.

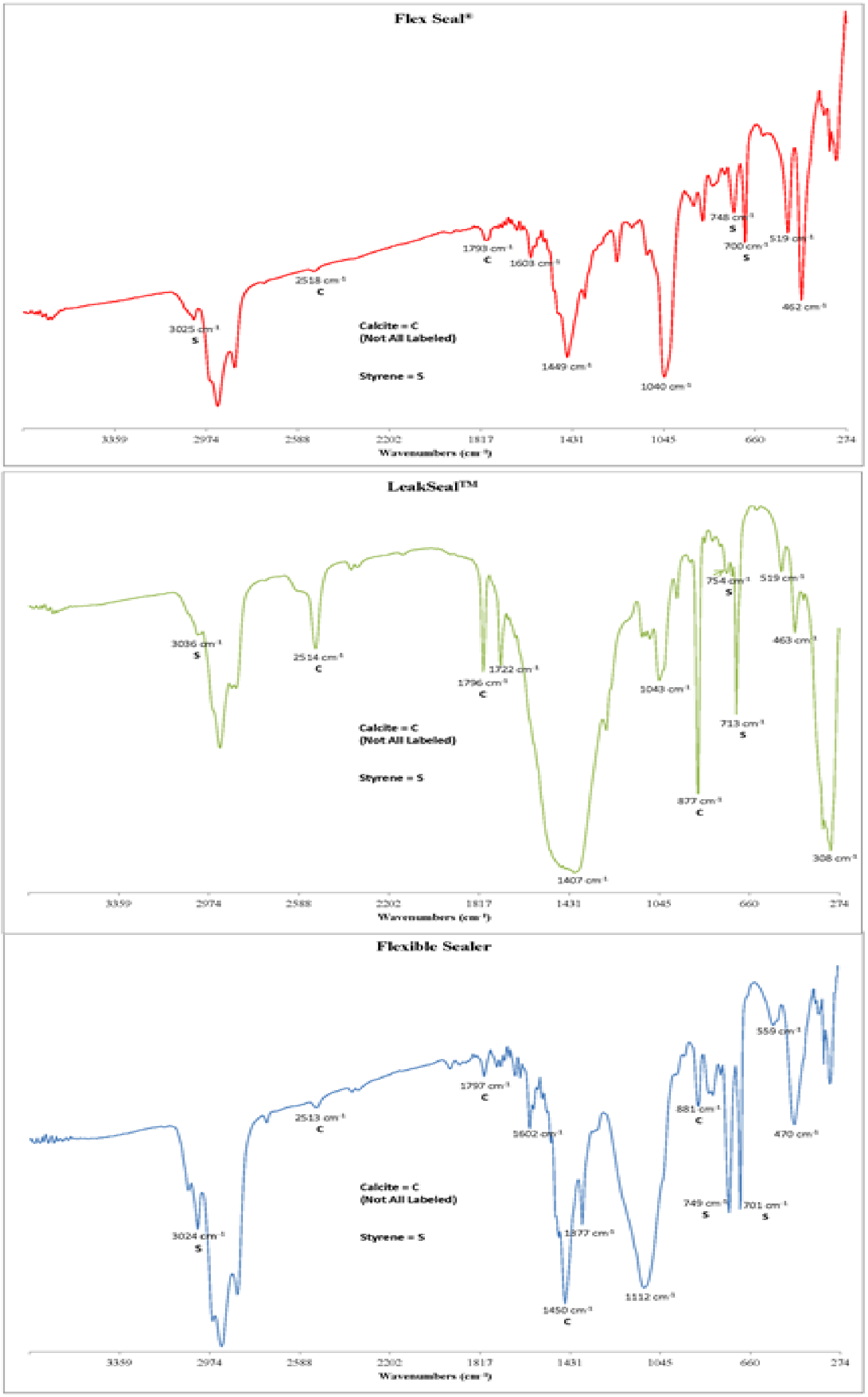

Figure 5 – IR spectra of Flex Seal®, LeakSeal™, and Flexible Sealer.

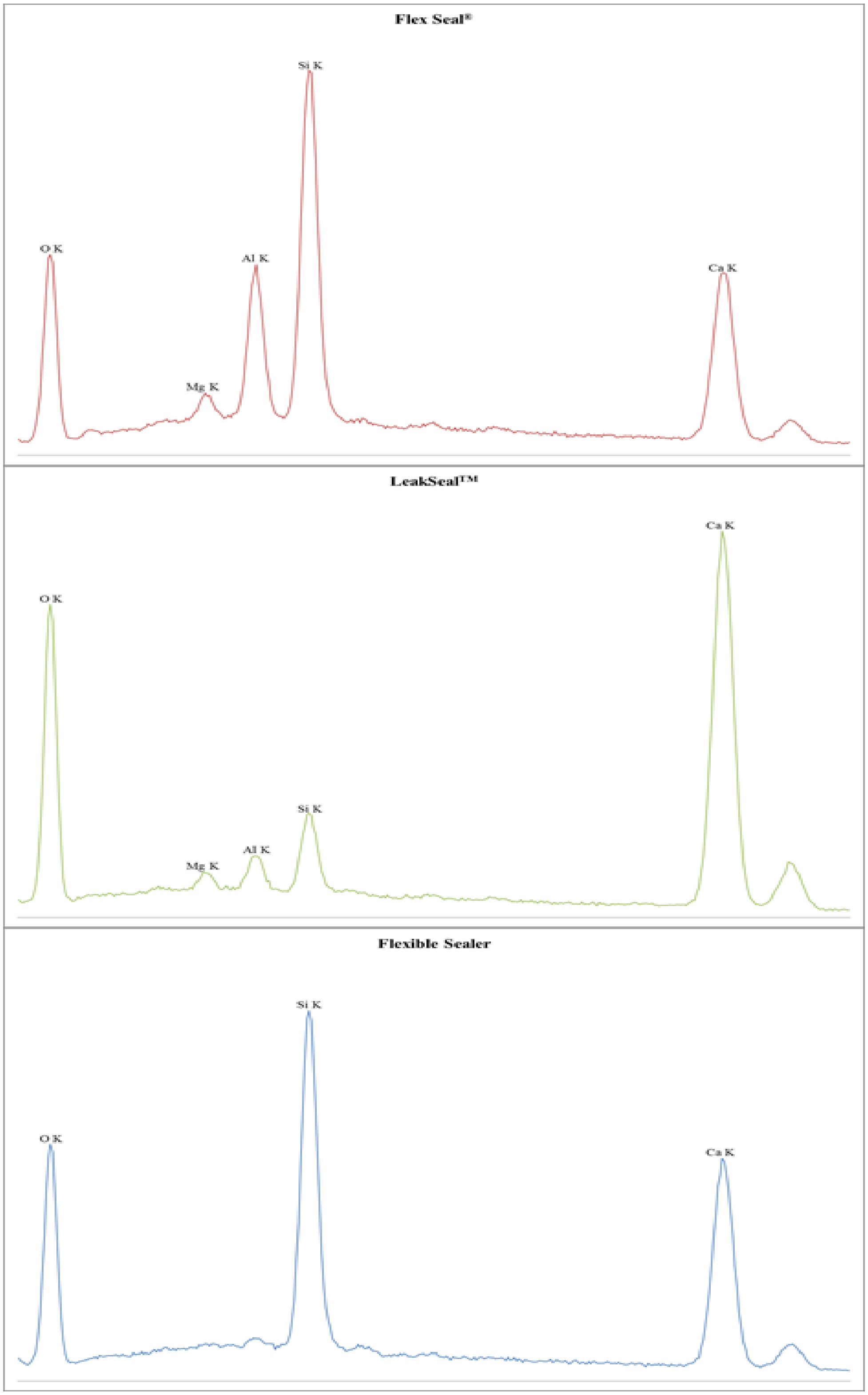

Figure 6 - Overall SEM-EDX of Flex Seal®, LeakSeal™, and Flexible Sealer. These spectra have been cropped to show the only peaks observed.

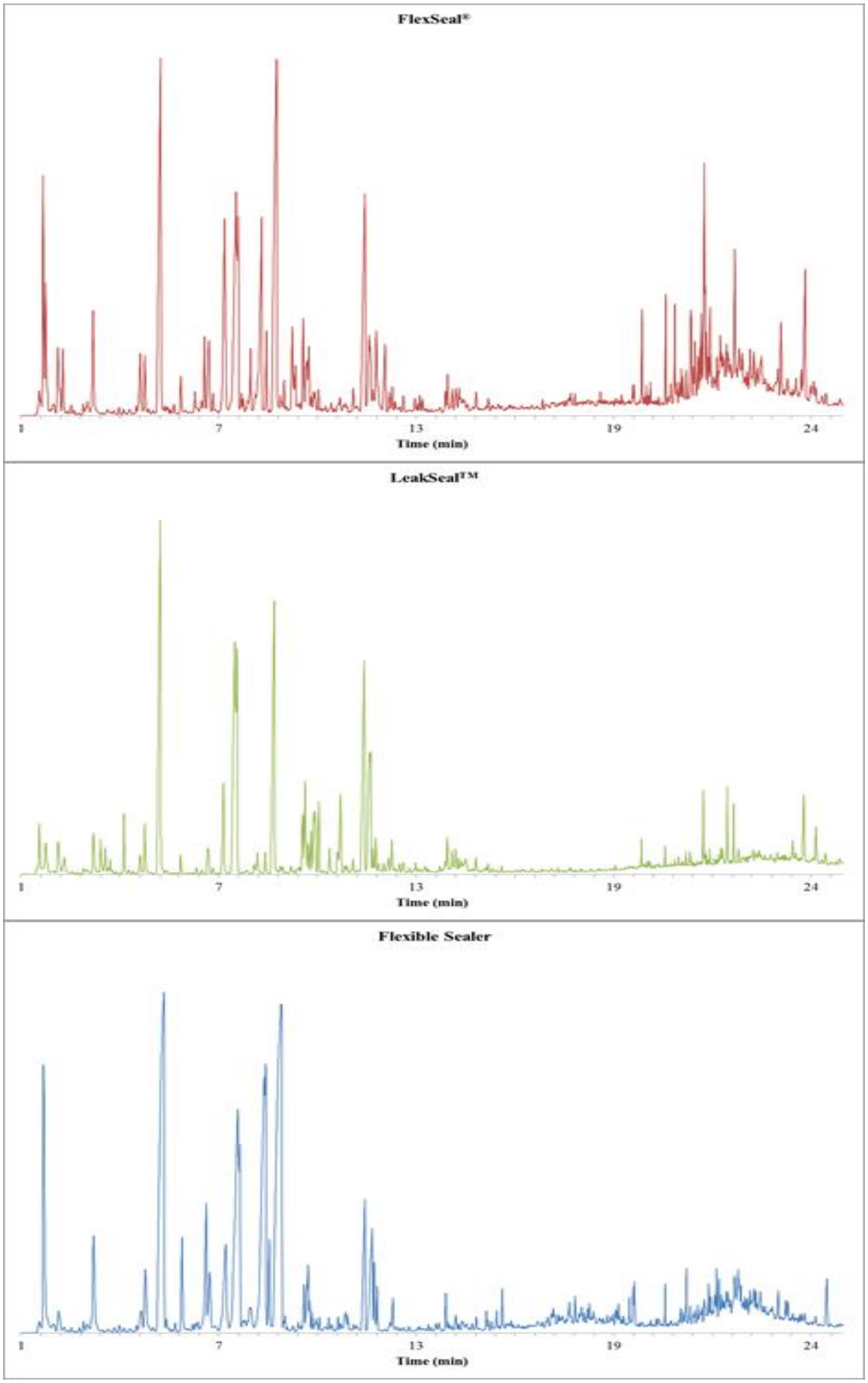

Figure 7 – Pyrogram of Flex Seal®, LeakSeal™, and Flexible Sealer (Styrene is the predominant peak just past five minutes in each of the spectra)

CONCLUSIONS

Analysis of the three brands of sealants showed that they consist of styrene, carbon black, calcite, silicates, and other various extenders. It is noted that compounds on some of the Safety Data Sheets such as barium sulfate, and hydrogen sulfide were not observed. Further analysis may reveal these compounds as they may be overshadowed by the extensive amounts of calcium carbonate. Based on the instrumental and optical analysis, it was possible to differentiate these three flexible sealants. LeakSeal™ displayed readily apparent differences from the other two sealants, while Flex Seal® and Flexible Sealer displayed more subtle differences from each other. These sealants are readily available and could be found in forensic examinations such as in this case or during an architectural paint comparison. Further studies could include investigations into their durability and chemical components over time and after being exposed to the environment.

REFERENCES

1. Flex Seal; Petrochem Manufacturing Inc.: Carlsbad, CA, March 14, 2006. http://pmitechnology.com/wp-content/uploads/2010/03/FlexSeal-NC-MSDS.pdf (accessed June 24, 2014).

2. LeakSeal; Rust-Oleum: Vernon Hills, IL, August 29, 2013. http://www.rustoleum.com/MSDS/ENGLISH/265495.PDF (accessed June 24, 2014).

3. Home Armor Flexible Sealer; W.M. Barr: Memphis, TN, October 15, 2013. http://www.homearmor.com/uploads/general/HA_Flexible_Sealer_Black.pdf (accessed June 24, 2014).

4. Winchell, Alexander Newton; Winchell, Horace. 1964. The Microscopical Characteristics of Artificial Inorganic Solid Substances: *Optical Properties of Artifical Minerals*. 3rd Edition. Chicago, IL (USA).