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Tubule Nanocontainers for Corrosion Inhibitors, *CMMI-1029147*

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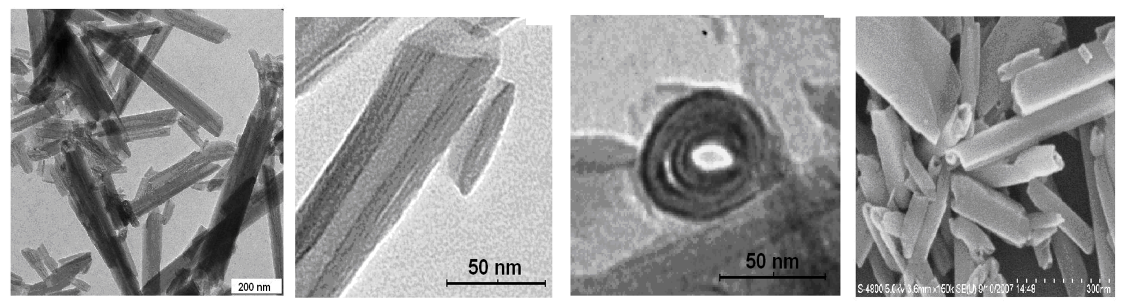
Abstract

Long lasting anticorrosive coatings for steel have been developed based on halloysite nanotubes loaded with corrosion inhibitors: benzotriazole, mercaptobenzothiazole and mercaptobenzimidazole. The inhibitors' loaded tubes were admixed at 5-7 wt % to alkyd paint providing sustained agents release and corrosion healing in the coating defects. Slow 20-100 hours release of the inhibitors in defect points caused remarkable improvement in anticorrosion efficiency. Further time expansion of anticorrosion agents release has been achieved by formation of release stoppers at nanotube-ends with urea-formaldehyde copolymer and copper-inhibitor complexation. Corrosion protection efficiency was tested on iron A365 alloy plates in 0.5 M NaCl solution with microscanning of corrosion current development, by microscopy inspection and studying paint adhesion. The best protection was found using halloysite / mercaptobenzimidazole and benzotriazole inhibitors.

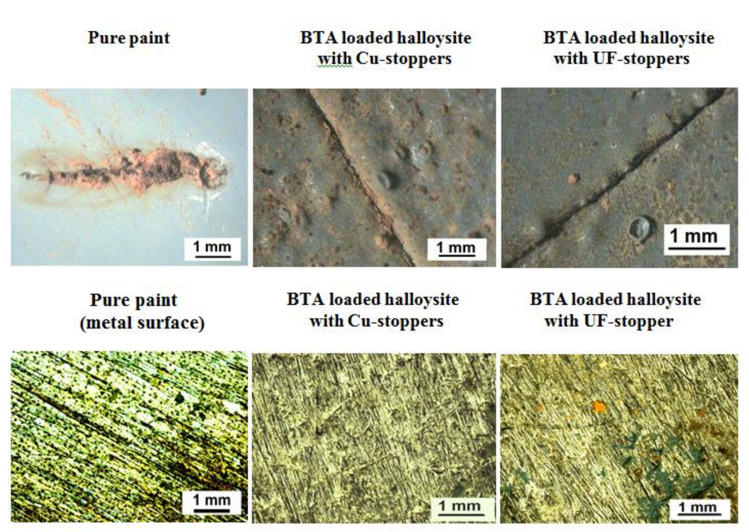
Halloysite nanotubes

Halloysite ($Al_2Si_2O_5(OH)_4$ x nH_2O) is a two-layered (1:1) aluminosilicate which exhibits a hollow tubular structure in the submicron range, and it is chemically similar to kaolin. The size of halloysite tubules varies within 0.5-1.5 microns of length, ca 15 nm of inner diameter and ca 50 nm of external diameter. There are 15-20 aluminosilicate layers rolled in the multilayer tubule walls with a layer spacing of 0.72 nm for the dehydrated halloysite.

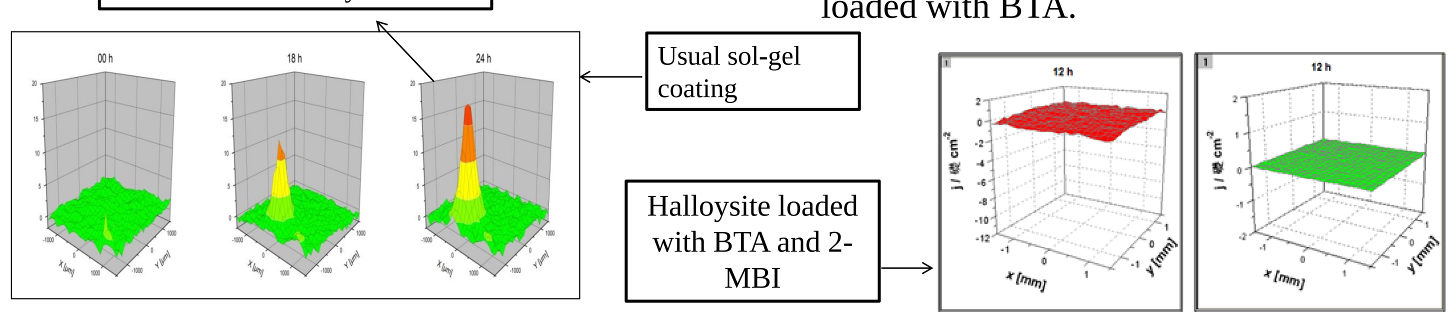


(a) (b) (c) (d)

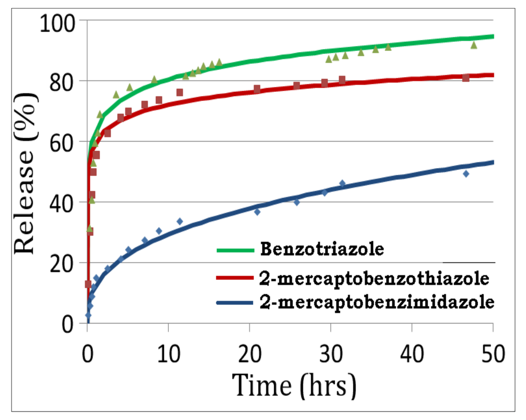
Transmission (a, b, c: tube cross-section) and scanning (d) electron microscopy images of halloysite nanotubes.



Metal surface by pulling out and the interface was analyzed using optical microscope to study formation of steel rust under the coating. In case of original paint, the metal surface has many brown spots indicating pitting undercoat corrosion process. Some of the rust was attached to paint and removed with it. Metals coated with halloysite based composite coatings had lesser corrosion spots indicating corrosion inhibition in all the cases. In order to check the influence of stoppers on corrosion rate, BTA loaded halloysite samples were encapsulated with both UF and Cu-BTA stoppers and doped into paint. Results from undercoat corrosion indicate much lesser rust formation in both the cases of stopper formation compared to uncapped halloysites loaded with BTA.

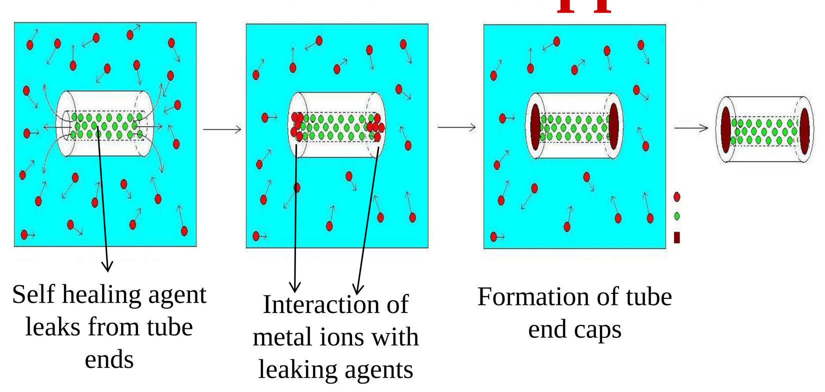


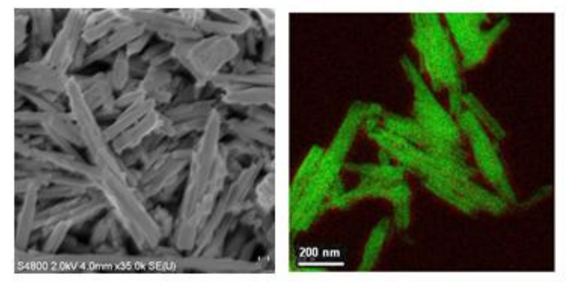
Self healing agents release characteristics



Release profiles of three corrosion inhibitors; benzotriazole, 2-mercaptobenzothiazole and 2-mercapto-benzothiazole from halloysite are shown. Release rates of benzotriazole and 2-mercapto-benzothiazole are close to each other more than 80% being within 40 hours while release rate of 2-mercaptobenzimidazole is a bit slower (only 50% in 50 hrs). Loading efficiencies of the inhibitors were 4.0 %, 8.0% and 20.0% by weight for benzotriazole, 2-mercaptobenzothiazole and 2-mercaptobenzimidazole respectively. High loading efficiency of the 2-mercaptobenzimidazole indicates that significant amount of the inhibitor was loaded into the tube.

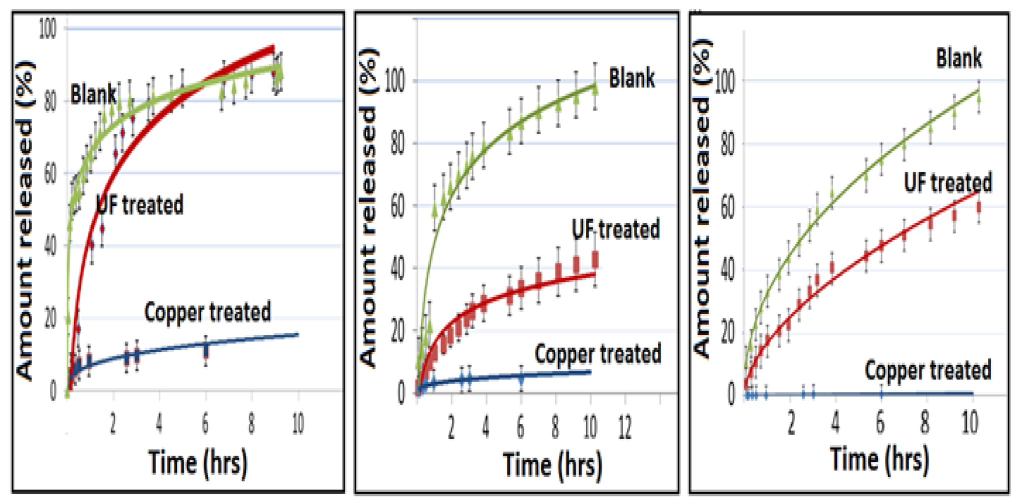
Tube end stoppers for controlled release





SEM of halloysite with UF-stoppers (left) and 2-MBI loaded halloysite with Cu stoppers (Cu elemental mapping using TEM)

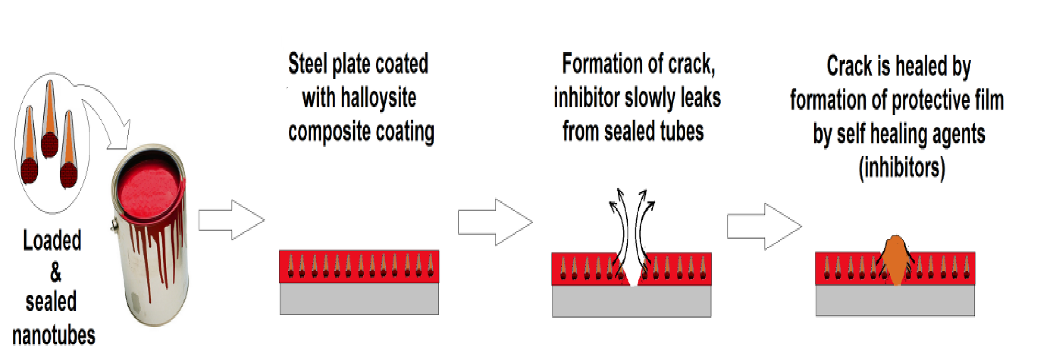
Controllable of self-healing agents from halloysite nanotubes is achieved by formation of caps at halloysite tube endings by interaction of leaking agents and metal ions from the bulk solution. The suggested method requires only short rinsing of loaded halloysite nanotubes with aqueous solution containing metal ions. Corrosion inhibitors like benzotriazole, benzimidazole, benzothiazole , etc forms stable 2-D complexes with most of the transition metal like copper. Polymeric stoppers like urea-formaldehyde were also proved to be effective for the controlled release of corrosion inhibitors by acting as stoppers.

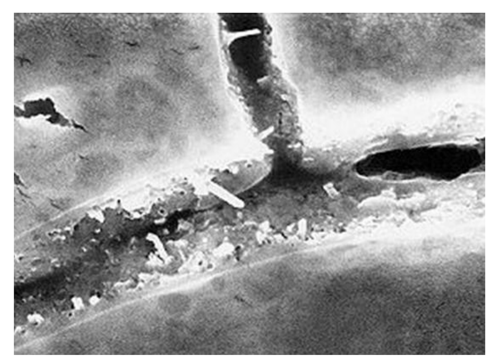


a b c

Fig. on the left is of release profiles for three different corrosion inhibitors BTA, 2-MBT and 2-MBI respectively. It was observed that halloysite samples with Cu and urea-formaldehyde (UF) stoppers reduced the rate of corrosion inhibitors release to some extent than the halloysite samples without stoppers. Copper stoppers were found to be more effective than UF stoppers.

Anticorrosive paint

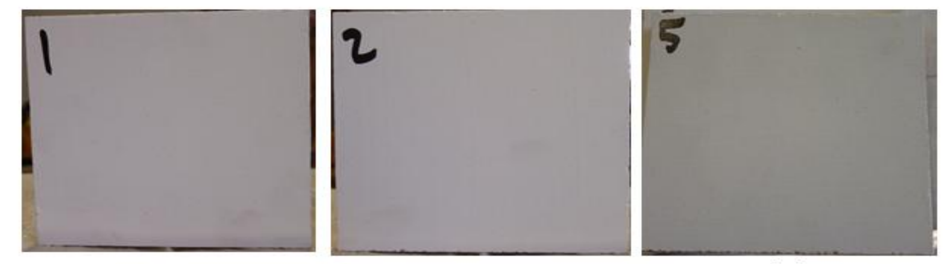




Halloysite nanotubes standing at the paint scratch, taken by SEM

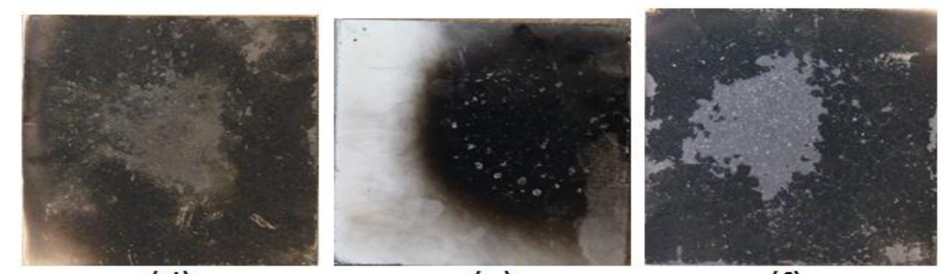
The idea behind corrosion resistant paint is to mix halloysite particles, that are preliminary loaded with corrosion inhibitors, with the paint. Halloysite can be readily mixed with water and oil based paints. Once crack formed in the paint, halloysite gets exposed to the corrosion environment by slowly releasing loaded self healing agents that fill the crack and resume protective function of the coating.

Application of halloysite as flame retardant



(a) (b) (c)

Pure latex paint (a), latex paint with 5 wt% halloysite (b) and paint with FR-1 flame retardant loaded halloysite (c) before flame testing

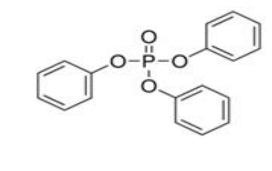


(d) (e) (f)

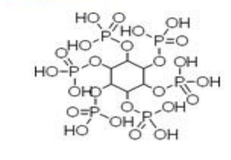
Pure latex paint (d), latex paint with 5 wt% halloysite (e) and paint with FR-1 flame retardant loaded halloysite (f) after flame testing

FR-1 flame retardant paint additive

To be used in the future



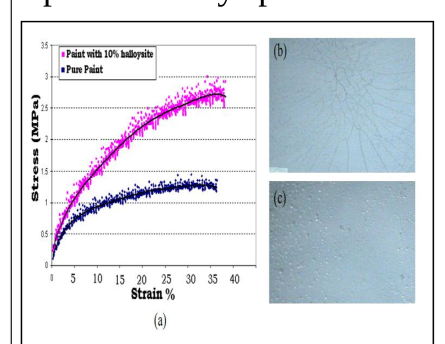
Triphenyl phosphate

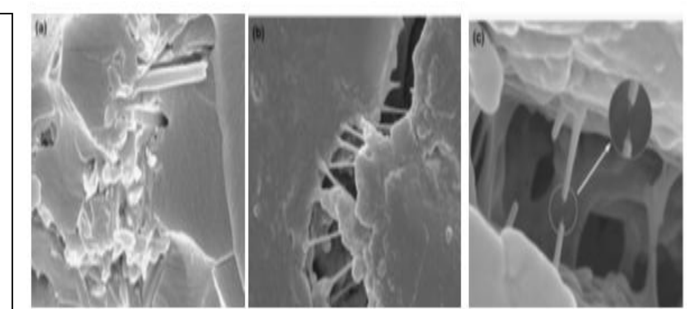


Phytic acid dipotassium salt

Halloysite-paint composite properties

Halloysite is readily mixed with a variety of metal protective coatings, which is an important advantage of this material. Contact angle of the paint droplet on halloysite pressed in the tablet was found to be as low as 3°. The paint droplet spontaneously spreads over a halloysite tablet, which is an indication of the good wettability of the halloysite by paint.





SEM of the fracture surfaces of the nanocomposites with 3 wt halloysite:
(a) nanotube debonding/ pull-out,
(b) nanotube bridging,
(c) nanotube fracture

Addition of nanotubes into industrial oil-based paint based on ECS-34 powder (Tru-Test Co.) significantly improved the strain-stress characteristics of the coating. 3-fold increase in paint tensile strength was observed with addition of 5 wt % halloysite (0.7 MPa for pure paint versus 1.9 MPa for 5 wt% halloysite-loaded paint). Addition of halloysite also improved the impact strength of paint to rapid deformations (ASTM D 2794 standard).

Conclusion

Natural clay nanotubes were employed as inexpensive containers offering essential benefits for the entrapment of corrosion inhibitors into metal coatings. Corrosion was retarded at the initial stage due to the inhibitive action of the benzotriazole, mercaptobenzothiazole and mercaptobenzimidazole slowly released from halloysite in response to coating defects. Minimal undercoat corrosion and best paint adhesion was obtained for mercaptobenzimidazole-halloysite coatings. Controlled sustainable release of the inhibitors was developed through urea-formaldehyde and copper - inhibitor complex formation at the tube ends. Microscan mapping of corrosion current on artificially scratched coating accomplished with visual observations of the developed corrosion spots showed that the paint with inhibitors loaded halloysite encapsulated with urea-formaldehyde-allowed for the most significant improvement in corrosion inhibition (no corrosion for 12 months).

References

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