

Less-Toxic Coatings for Inhibiting Corrosion of Aluminum

It is no longer necessary to use highly toxic and carcinogenic chromates.

John F. Kennedy Space Center, Florida

Two recently invented families of conversion-coating processes have been found to be effective in reducing or preventing corrosion of aluminum alloys. These processes offer less-toxic alternatives to prior conversion-coating processes that are highly effective but have fallen out of favor because they generate chromate wastes, which are toxic and carcinogenic. Specimens subjected to these processes were found to perform well in standard salt-fog corrosion tests.

One family of processes is based on the treatment of suitably prepared aluminum-alloy workpieces with calcium hydroxide (lime) solutions. Preparation of a workpiece usually includes the following steps: (1) degreasing (e.g., by use of a solvent), (2) cleaning by use of a commercially available alkaline solution, (3) rinsing in water, (4) treatment with a commercially available deoxidizing solution, and (5) optionally coating with boehmite [$\text{AlO}_x(\text{OH})_y$] and with transition-metal oxyanions that can include molybdates and/or permanganates, among others. The prepared workpiece is then treated in an aqueous conversion solution that contains between 0.06 and 0.15 weight percent of $\text{Ca}(\text{OH})_2$ plus between 0.4 and 5 weight percent of alkali-metal nitrates. Typically, this treatment lasts between 2 and 20 minutes, during which the temperature of the solution is maintained between 50 and 100 °C.

The success of the process depends on the use of a freshly prepared conversion solution: The solution should be made by use of deionized water and should be heated to the treatment tem-

perature before adding the $\text{Ca}(\text{OH})_2$. Immediately before immersing the workpiece in the solution, the required amount of $\text{Ca}(\text{OH})_2$ should be added.

Optionally, the workpiece can be post-treated to seal the conversion coat and contribute some additional resistance to corrosion. Suitable post-treatment sealing solutions include silicates, borates, and phosphates of alkali metals. The concentrations of the solutes in the sealing solutions can range from 0.05 to 10 weight percent, treatment times can range from 2 to 10 minutes, and treatment temperatures can range from 50 to 80 °C. Finally, the workpiece is rinsed with deionized water, then dried in air for several days.

The other family of processes is based on the treatment of suitably prepared aluminum-alloy workpieces with conversion solutions that contain molybdate (MoO_4^{2-}) ions. The preparation of a workpiece for a process in this family is similar to that for a $\text{Ca}(\text{OH})_2$ conversion-coating process: The workpiece is degreased and otherwise cleaned, deoxidized, and coated with boehmite. The prepared workpiece is then treated in an aqueous conversion solution that contains between 1 and 3 weight percent of molybdate ions plus, optionally, small percentages of any or all of the following ingredients: fluorides, oxyanions associated with high-valence transition-metal cations, silicates, borates, phosphates, and/or nitrates. Typically, the treatment lasts between 1 and 60 minutes, during which the temperature of the conversion solution is maintained between 25 and 100 °C and the pH of

the solution is maintained between about 10 and 12, the exact value depending on the composition of the solution.

As in the family of $\text{Ca}(\text{OH})_2$ conversion-coating processes described above, the workpiece can be post-treated to seal the conversion coat and increase resistance to corrosion. One suitable post-treatment process involves the use of a $\text{Ca}(\text{OH})_2$ conversion-coating solution as described above. Other suitable post-treatment solutions include silicates, borates, and phosphates of alkali metals — solutions like those mentioned above for post-treatment following $\text{Ca}(\text{OH})_2$ conversion coating. The concentrations of the solutes in these sealing solutions can range from 4 to 10 weight percent, treatment times can range from 5 to 20 minutes, and treatment temperatures can range from 25 to 98 °C. Then, as described above, the post-treated workpiece is rinsed in deionized water and dried in air.

This work was done by Zoran Minevski, Eric Clarke, Cahit Eylem, Jason Maxey, and Carl Nelson of Lynntech, Inc., for Kennedy Space Center.

In accordance with Public Law 96-517, the contractor has elected to retain title to this invention. Inquiries concerning rights for its commercial use should be addressed to:

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Refer to KSC-12114/15, volume and number of this NASA Tech Briefs issue, and the page number.

Liquid Coatings for Reducing Corrosion of Steel in Concrete

Structures could be protected more easily and less expensively.

John F. Kennedy Space Center, Florida

Inorganic coating materials are being developed to slow or stop corrosion of reinforcing steel members inside concrete structures. It is much simpler and easier to use these coating materials than it is to use conventional corrosion-inhibiting systems based on impressed electric currents. Unlike impressed

electrical corrosion-inhibiting systems, these coatings do not require continuous consumption of electrical power and maintenance of power-supply equipment. Whereas some conventional systems involve the use of expensive arc-spray equipment to apply the metallic zinc used as the sacrificial

anode material, the developmental coatings can be applied by use of ordinary paint sprayers.

A coating material of the type under development is formulated as a liquid containing blended metallic particles and/or moisture-attracting compounds. The liquid mixture is sprayed onto a con-

crete structure. Experiments have shown that even though such a coat resides on the exterior surface, it generates a protective galvanic current that flows to the interior reinforcing steel members. By effectively transferring the corrosion process from the steel reinforcement to the exterior coating, the protective current slows or stops corrosion of the embedded steel. Specific formulations have been found to meet depolarization criteria of the National Association of Corrosion Engineers (NACE) for complete protection of steel reinforcing bars ("rebar") embedded in concrete.

A coating of this type can be applied thick enough to afford protection for ten years or longer. The coating can easily be maintained or replaced to ensure continued protection of the reinforcing steel for an indefinite time.

The costs of protecting structures by use of these coating materials are expected to be less than (or in some cases, comparable to) the costs of protection

by most conventional methods:

- Typical costs of installing impressed-current systems range from 10 to 30 dollars per square foot (about 110 to 330 dollars per square meter) [prices as of year 2000]. After installation, these systems incur additional costs of electrical power, inspection, and maintenance.
- The costs of installing sacrificial systems based on thermally sprayed zinc typically range between 10 and 20 dollars per square foot (about 107 to 215 dollars per square meter). Like the present developmental systems, sacrificial-zinc systems require very little maintenance once they are installed.
- Another type of sacrificial system involves the use of zinc sheet and electrically conductive glue. The costs of installing these systems typically range from 8 to 18 dollars per square foot (about 86 to 194 dollars per square meter). These systems also require very little maintenance after installa-

tion. Both this and the preceding sacrificial-zinc system have been said to offer 10-year life expectancy. However, according to NACE, pure zinc coats on concrete structures provide only partial protection because of their low driving voltages. Upon exposure, the zinc can become passivated, such that during dry weather, it does not supply protective current to steel rebar.

- The costs of protecting structures by use of the developmental coating materials have been estimated to range from 5 to 9 dollars per square foot (about 54 to 97 dollars per square meter).

This work was done by Louis G. MacDowell of Kennedy Space Center and Joseph Curran of Dynacs, Inc.

This invention is owned by NASA, and a patent application has been filed. Inquiries concerning nonexclusive or exclusive license for its commercial development should be addressed to the Technology Programs and Commercialization Office, Kennedy Space Center, (321) 867-8130. Refer to KSC-12049.

Processable Polyimides Containing APB and Reactive End Caps Properties can be tailored through choice of proportions of dianhydrides and APB.

Langley Research Center, Hampton, Virginia

Imide copolymers that contain 1,3-bis(3-aminophenoxy)benzene (APB) and other diamines and dianhydrides and that are terminated with appropriate amounts of reactive end caps have been invented. The reactive end caps investigated thus far include 4-phenylethynyl phthalic anhydride (PEPA), 3-aminophenoxy-4'-phenylethynylbenzophenone (3-APEB), maleic anhydride (MA), and 5-norbornene-2,3-dicarboxylic anhydride [also known as nadic anhydride (NA)]. The advantage of these copolyimides terminated with reactive groups, relative to other polyimides terminated with reactive groups, is a combination of (1) higher values of desired mechanical-property parameters and (2) greater ease of processing into useful parts.

Homopolymers that contain only other diamines and dianhydrides and that are not processable under conditions reported previously can be made processable by incorporating various amounts of APB according to this invention, depending on the chemical structures of the diamines and dianhydrides used. These copolyimides exhibit high degrees of resistance to sol-

vents, high glass-transition temperatures, and high moduli of elasticity, but are processable at low pressures [≤ 200 psi (≤ 1.38 MPa)], when the appropriate amounts of APB are utilized. In addition, when these copolymers are terminated with phenylethynyl groups, they exhibit long-term melt stability (several hours at temperatures approaching 300 °C).

The dianhydride incorporated into a polymer of this type has a rigid molecular structure that tends to degrade processability. The addition of the highly flexible APB diamine improves processability, while the imide structure provides stiffness to the polymer backbone, increases resistance to solvents, and improves mechanical properties. The resulting combination of properties is important for the use of the copolymer as a matrix in a composite material or as an adhesive or a film, coating, or molding material: If too little APB is incorporated into the polymer backbone, the resulting material is not processable under desired processing limitations. If too much APB is incorporated into the polymer backbone, the resulting material becomes highly

flexible with a lower glass-transition temperature than desired.

Hence, by choosing the ratio between the amount of APB and the amount of the other diamine in the polyimide backbone, one can obtain a material that has a unique combination of solubility, glass-transition temperature, melting temperature, melt viscosity, toughness, and high-temperature mechanical properties. The exact amount of APB needed to optimize this combination of properties is not predictable and must be determined for the intended application and for the proposed method of processing the copolymer for use in the application.

This work was done by Brian J. Jensen of Langley Research Center. Further information is contained in a TSP (see page 1).

This invention has been patented by NASA (U.S. Patent No. 6,133,401). Inquiries concerning nonexclusive or exclusive license for its commercial development should be addressed to Greg Manuel, Technology Commercialization Program Office, Langley Research Center, MS 200, Hampton, VA 23861, g.s.manuel@larc.nasa.gov. Refer to LAR-15449.