

Analysis of Influence of Snow Melting Agents and Soil Components on Corrosion of Decorative Chrome Plating

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ABSTRACT

The dissolution and exfoliation of chromium plating specific to Russia was studied. Investigation and analysis of organic compounds in Russian soil revealed contents of highly concentrated fulvic acid. Additionally, it was found that fulvic acid, together with CaCl_2 (a deicing agent), causes chromium plating corrosion. The fulvic acid generates a compound that prevents reformation of a passivation film and deteriorates the sacrificial corrosion effectiveness of nickel.

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INTRODUCTION

As the global automobile market grows, an increasing number of cars are used in areas where there is a highly corrosive environment. Decorative chromium plating for automobile exterior coatings is used on parts of the vehicle that are important with regard to the strong impact that they have on brand image and design properties. For this reason, improving anti-corrosiveness and maintaining a high quality appearance is critical.

In Russia, where the automobile market is expanding, chromium plating sometimes suffers from a specific type of corrosion. Calcium chloride (CaCl_2), a de-icing agent, is sprayed in large quantities during winter in Russia, and is a suspected cause of this corrosion. Calcium chloride produces chloride ions at high concentration, giving chromium a lower potential than that of nickel, and probably causing the creation of a nickel-chromium cell containing a dense calcium chloride solution that dissolves the chromium [1].

An experiment to reproduce chromium dissolution-corrosion was performed by simulating a brine mud environment using calcium chloride and kaolin [2], resulting in dissolution-corrosion of the chromium being reproduced. However, the reason that the corrosion occurs specifically in Russia is not yet clear, since calcium chloride is sprayed for the purpose of melting snow in many other areas.

A study was carried out to explore the causes of the chromium corrosion that specifically occurs in Russia, and the mechanism of corrosion of the chromium plating was determined. This report describes the results.

SURVEY OF RUSSIAN SOIL

Many roads in Russia are not paved, and therefore a large amount of soil deposits on the surface of the vehicle body. Since a large quantity of de-icing agent is sprayed in winter when calcium chloride is

scattered, it comes into contact with the vehicle and adheres strongly to the vehicle body following repeated cycles of drying and wetting in the air, and consequently causes the chromium plating to become corroded. A survey of de-icing agent components and types concluded that there are no large differences between those in Russia and other areas. In this study, a different survey was conducted focusing on Russian soil.

First, corrosive inorganic compounds, soluble ions, and particle size distributions in the soil were analyzed, and the properties of Russian soil were compared with those of the soil in other countries. However, no special properties were found in Russian soil.

Next, in the course of a geological and pedological survey, a report was found in a soil database [3] which stated that Russian soil belongs to an organic soil area, and that its organic soil components are mainly composed of bulky organic and humic organic matter, humic substances being especially reactive with metals [4].

Humic substances include two types of organic acids: fulvic acid (Figure 1) and humic acid (Figure 2). Figures 1 and 2 below illustrate their structure [5].

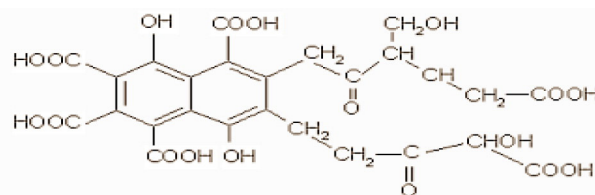


Figure 1. Fulvic acid structure

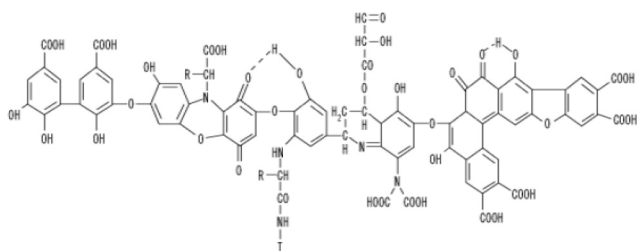


Figure 2. Humic acid structure

Fulvic and humic acid are acidic organic compounds contained in peat and lignite, which are types of humic soil. From a survey on the difference between fulvic and humic acid, it is known that fulvic acid dissolves in both acidic and neutral solvents, and that all of its functional groups give rise to cation exchange reactions. In addition, it forms a complex with metals [6].

Given the properties of fulvic acid, it is probable that the corrosion of chromium plating is caused by a sequence of reactions such as the following: the calcium chloride sprayed in large quantities in Russia and the fulvic acid in Russian soil give rise to an ion exchange reaction which generates hydrochloric acid and thereby reduces the pH value; fulvic acid bonds with chromium (to form a complex) giving rise to changes in chromium passivation film properties; and changes occur in the sacrificial protection effect of the plating film.

Based on the soil survey and the properties of fulvic acid, and assuming that the proposed mechanism of corrosion is responsible, the organic soil areas (Figure 3) listed in the soil database [3], highly ion-exchange prone soil areas (Figure 4), and highly acidic soil areas (Figure 5) were examined. The results show that Russian has many areas satisfying all these conditions, with many located in Moscow.

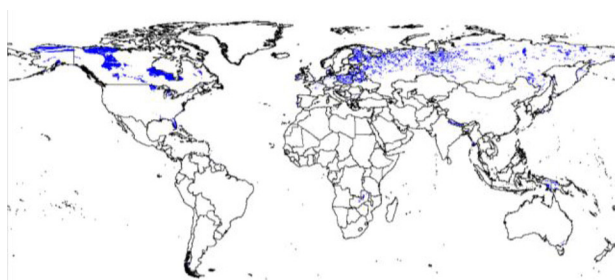


Figure 3. Area of soil containing highly concentrated organic compounds

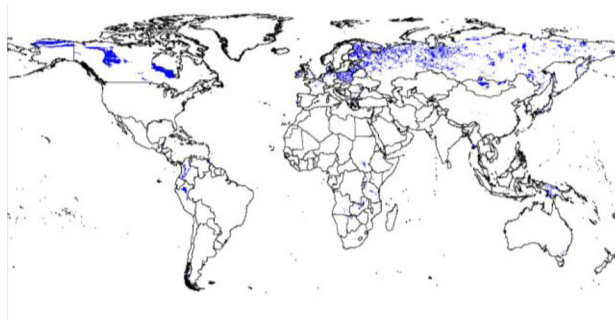


Figure 4. Ion-exchangeable soil area

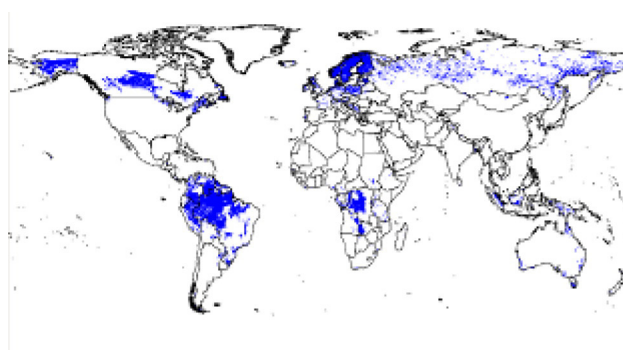


Figure 5. Highly acidic soil area

Soil samples were collected from some of the areas in Russia, America, Canada, and Japan shown in Figures 3, 4, and 5, and analysis was performed. Figure 6 shows the results. Up to 11 mass% of fulvic acid was detected in the soil from Russia. This shows that Russian soil contains more fulvic acid than that in other areas.

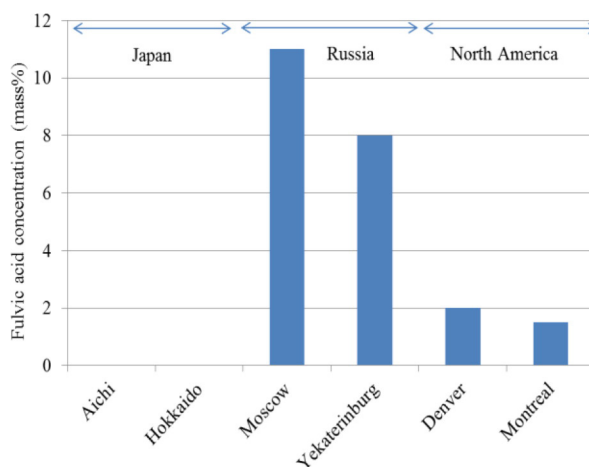


Figure 6. Fulvic acid concentration in soil

The soil survey and analysis revealed that high fulvic acid content is a property specific to Russian soil. The authors performed the following experiments in order to examine the relationship between fulvic acid and the corrosion of chromium plating.

EXPERIMENTAL METHOD

Pre-Test: Comparison between the Effect of Fulvic Acid and Humic Acid on the Corrosion of Chromium Plating

Since fulvic and humic acid, which are humic substances, possess different properties, it is probable that they have a different effect on the corrosion of chromium plating. In order to select the more corrosive acid for the test, a pre-test was conducted to discover whether fulvic or humic acid has the larger effect on corrosion.

The test pieces were trivalent chromium plating films made using a trivalent chromium plating bath with chromium sulfate as the source.

A solution of calcium chloride and fulvic acid and a solution of calcium chloride and humic acid were prepared. Each of these test solutions was applied to each test piece, which was then dried.

The raw fulvic acid used here was artificially extracted from a cultured plant, and the humic acid reagent was made by Nacalai Tesque.

Two sets of base solution were prepared, each consisting of ten grams of calcium chloride dissolved in 50 mL of water, and then 30 g of fulvic acid was added to one and 30 g of humic acid to the other to give the test solutions.

The test pieces to which solvent had been applied were dried in a 60°C 30% RH environment for two weeks. Following this, the dried mud was removed and the chromium plating surfaces visually examined.

Main Test: Comparison of Chromium Plating Corrosion Conditions

The organic acid which was determined in the pre-test of the previous section to be the more corrosive was selected, and this acid was used to test the effect on the corrosion of chromium plating.

The test pieces were covered with a trivalent chromium plating film created using a trivalent chromium plating bath with chromium sulfate as the source.

The test pieces were subjected to three types of corrosion test conditions, as follows: (1) chromium plated automobile parts were installed on a vehicle, which was then run for monitoring purposes for two years in Moscow, Russia; (2) 10 g of calcium chloride was dissolved into 50 mL of water, 30 g of kaolin was mixed in, the resulting solution was applied to the test pieces, and the test pieces were then placed in a 60°C, 30% RH environment for two weeks; and (3) 10 g of calcium chloride was dissolved into 50 mL of water, and, after 30 g of kaolin had been added, 11 mass% of the organic acid- the same as the percentage result obtained from analysis of Russian soil -was mixed in and the resulting mixture applied to the test pieces, which were then placed in a 60°C, 30% RH environment for two weeks.

The mud was removed from these test pieces after the test had ended. Elemental analysis of the corroded areas was performed with an electron probe micro-analyzer (EPMA), test piece cross-sections were observed with a field emission scanning electron microscope (FE-SEM), and test piece cross-sections and corresponding element distributions were analyzed using a scanning electron microscope (SEM) and its ancillary energy dispersive X-ray analyzer (EDX)

EXPERIMENTAL RESULTS

Pre-Test: Comparison of the Effect of Fulvic Acid and Humic Acid on the Corrosion of Chromium Plating

Figure 7 shows the effect of fulvic acid and humic acid on corrosion of the chromium plating.

The tests using fulvic acid produced corrosion of the chromium plating, while those using humic acid produced only slight corrosion at the borderline between the applied mud and chromium film, with corrosion over the whole area not occurring. This shows that fulvic acid contributes more to the corrosion of chromium plating than humic acid. For test pieces tested in the same manner after application of a solution containing only fulvic acid or only calcium chloride, no corrosion was found. These results show that the presence of both fulvic acid and calcium chloride are required for the occurrence of this specific type of corrosion.

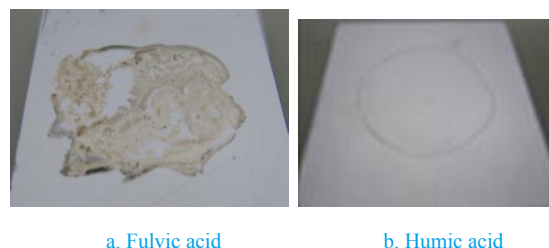


Figure 7. Comparison of samples after the corrosion test

Main Test: Comparison of Chromium Plating Corrosion Conditions

EPMA elemental analysis of the chromium coating and SEM-EDX observation of cross-sections of the corroded areas were conducted using the following samples: (1) the trivalent chromium plated part installed in the monitoring vehicle in Russia, (2) a trivalent chromium plated test piece painted with brine mud (a solution of calcium chloride and kaolin), and (3) a trivalent chromium plated test piece painted with brine mud mixed with fulvic acid.

EPMA Elemental Analysis of Chromium Plating Surface

Figures 8, 9, and 10 show the results of EPMA surface element analysis of test pieces (1) to (3).

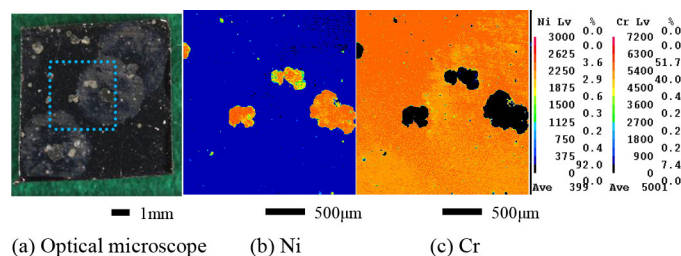


Figure 8. EPMA results of Cr plating films from Russian monitoring

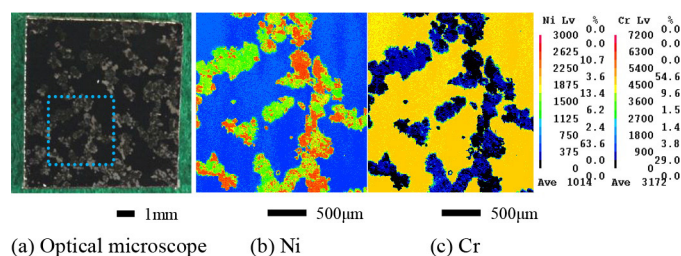


Figure 9. EPMA results of Cr corrosion test using kaolin