Formation and Removal of Silicon Ion Deposits on Glass and Metal Surfaces

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ABSTRACT: Scale-like dirt (ion deposit) occurs on glass surfaces of buses and trains after rain or vehicle washing, as various ionic substances are in the rain and tap water. Ion deposits blur the glass, leading to degraded passenger service. Removal of ion deposits is not possible with a general cleaner. The formation behaviour of ion deposits was examined in order to develop a quick cleaning method of glass surfaces of vehicles. Ion deposits form due to silicon ions in the water. Ion deposits and glass surfaces have strong adhesion. Analysis of laser Raman spectroscopy revealed that ion deposits are mainly composed of silicon and are almost the same compound as glass. Ion deposits could be removed with a low concentration of hydrofluoric acid, and it was possible to remove about 1 mg of ion deposit by using 1 mL of 0.5% hydrofluoric acid.

KEY WORDS: ion deposit, glass, metal, surface, laser Raman spectroscopy, SEM [D3]

1. Introduction

It is well known that water droplet marks (generally called water deposits or water spots, hereinafter referred to as ion deposits) are formed on glass windows of cars, buses and trains. The ion deposits are fixed to the glass surface in the form of white rings, as shown in Fig. 1, and removal work is periodically performed because it affects the appearance of the vehicle and the driver’s visibility, as well as passenger service (1). Ion deposits cannot be removed by wiping with water or detergents such as surfactants. A cleaning method using strong acid and polishing with a compounding agent are generally used for removing ion deposits from the surface of glass (2). However, cleaning with strong acid may have exposure accidents, and it is very dangerous to handle. In additions, the polishing method requires effort, and it scrapes not only the ion deposits but also the entire surface of the glass. It is known that the formation of ion deposits is due to ionic substances in the water generated after rain and vehicle washing. There is also a method of washing with water with non-ionic substances to prevent the formation of ion deposits (3). However, the period of the filter is short and thus it needs to be replaced frequently. It is also impossible to remove adhered ion deposits, since it is only an anti-fouling method. Hence, the development of a simple removal method and a technique to prevent ion deposits are required.

There are very few reports on the formation of ion deposits on the glass of vehicles. One study investigated the appearance of white turbidity on multi-layer polycarbonate glass used on Shinkansen trains (1) and another study investigated a method for removing and preventing white turbidity (2). There are no reports on research into the formation behaviour of ion deposits and their composition from a scientific point of view.

In this study, experiments on ion deposits and chemical composition analysis were conducted in order to clarify the chemical structure, chemical formation mechanism and composition of ion deposits, and a rapid removal method was developed. This study contributes to the development of methods for removing and preventing ion deposits.

Fig. 1 Ion deposits formed on a bus window.

2. Materials and Methods

Ion deposits were produced on various surfaces such as glass, glass coated with automotive glass film and metals in order to examine the formation. Commercially available glass slides (soda–lime glass, 15 × 15 mm² and 1 mm thickness) for microscopic observation were used as a substrate. Soda–lime glass contains SiO₂ as the main component, along with Na₂O, CaO and MgO (4), and is widely used not only for cars but also for buildings. The glass surfaces without any application and with 3 types of automotive glass film from the market were prepared as coating surfaces for ion deposits. Hard-coat film (LUMICOOL, 1501 UH, LINTEC), non-hard-coat film (LUMICOOL, 1501E, LINTEC) and rigid hard-coat film (ClearPlex, Madico Inc.) were used. Fig. 2 shows a cross-sectional view of the hard-coat glass film used in automobiles. As shown in Fig. 2, the hard-coat film consists of 3 layers: hard-coat, film and adhesive, and the hard-coat layer has the effect of suppressing scratches. In addition, aluminium plates (10 × 10 mm²
and 1 mm thickness) were also prepared as coating surfaces for ion deposits. Since ion deposits are also generated on car bodies and metal parts, productions of ion deposits on metal surfaces were also attempted.

Groundwater, tap water and rainwater collected from Toyohashi City (Japan) were used for the production of ion deposits in this study. In addition, silicon ion solution was prepared by stirring and filtering the silica sand (Showa Chemical) and distilled water. The concentrations of various elements in water and silicon ion solution were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES; P-4010, Hitachi).

The prepared groundwater, tap water and silicon ion solution were pipetted on each prepared coating surface. The solution-coated samples were dried at 313 K with a hot plate until the solution droplets were completely evaporated. The pipetting and drying (evaporation) processes were repeated 5 times. Then, ultrasonic cleaning was performed in distilled water to remove the water-soluble substances, and the production of ion deposits was complete. SEM-EDX (S-4300, Hitachi) was used to confirm the presence or absence of ion deposits on the coating surfaces. The composition of ion deposits was identified with laser Raman spectroscopy (inVia, Renishaw).

### 3. Results and Discussions

#### 3.1. Element Analysis of Various Water

Fig. 3 shows the analysis results of various element concentrations in groundwater, tap water and rainwater used in the production of ion deposits. All water contained Si, Na, K, Mg and Ca ions, but ammonium ions were detected only in rainwater. The concentrations of Si, Na, K and Mg ions in groundwater were the highest, and the concentration of Ca was relatively high. The concentration of each element in rainwater was the lowest. Each type of water contained a lot of other elements (5), but only the elements with high concentrations are shown here.

![Fig. 3 Elemental analysis of various types of water used in the production of ion deposits.](image)

#### 3.2. Formation of Ion Deposits on Various Surfaces

Table 1 shows the experimental conditions of the production of ion deposits on various surfaces. Fig. 4 shows an image of Si ion solution deposited on a glass slide.

| Coating surface | Type                  | Groundwater, tap water, rainwater, 16.95 ppm Si ion solution |
|-----------------|-----------------------|--------------------------------------------------------------|
| Solution        | Pipetting amount      | 10 µL                                                        |
|                 | Number of times       | 5                                                            |
| Evaporation temperature | 313 K                  |                                                               |

*Fig. 4 Deposition of Si ion solution on glass surface.*

SEM and SEM-EDX images (distribution of Si concentration) of ion deposit on a glass surface formed by tap water are shown in Fig. 5. The contour of the ion deposit, indicated by red arrows, formed in a ring shape, as shown in Fig. 5 (a) and 5 (c). Since the ion deposit was firmly bonded to the surface of the glass, it could not be easily removed even by ultrasonic cleaning with pure water or rubbing with a finger. It was found that Si was present, as shown in Fig. 5 (b) and 5 (d). The same analysis was performed on many samples and it was found that Si was the main element of ion deposits, regardless of the type of water. Moreover, all elements present in water (Na, Mg, K and Ca) were detected at low concentrations.

The evaporation of a water droplet is from a position farthest from the centre of the droplet, since it uniformly evaporates from a portion exposed to the outside air. The local evaporation rate of a water droplet can be calculated by the following equation:

\[
\frac{w_x}{x} = \frac{1}{x^{1/2}} \left( e_x - e \right) \times 10^{-3} \ [g/(cm^2 \cdot h \cdot hPa)]
\]

where \(x\) is distance from the contour to the centre of the water droplet; \(e_x\) is water vapour pressure at the evaporation surface; and \(e\) is water vapour pressure of air. This is a formula for the condition at a temperature of 288 K and standard atmospheric pressure, but there is almost no change in the constant of the formula if temperature is in the range of 273 K to 323 K and atmospheric pressure is in the range of 970 hPa to 1030 hPa. Moreover, it is a formula of laminar natural convection with a relatively small airflow. From the equation, the evaporation rate of the water droplet increases as the distance from the centre increases.
From the results of the experiments (especially compounds containing SiO₂ adhered to the glass surface as ion deposits) and the physical mechanism by which ion deposits are generated from droplets containing fine particles \(^{(7,8)}\), the chemical mechanism of the formation of ion deposits was estimated.

First, there is a process of generating fine particles in droplets. Evaporation of droplets starts from the edge, and humidity is supplied from the centre to the edge as evaporation occurs, so that weak Marangoni convention occurs inside the droplet \(^{(7)}\). The fine particles are generated by a chemical reaction between the elements contained in water and the flow of Marangoni convection in the evaporation process. As the free surface of the droplet breaks with evaporation, the fine particles are carried to the edge by convection in a ring shape and chemically bond to the surface of the glass \(^{(8)}\). This process is considered as the generation of anion deposit. The sequential reaction of the formation of fine particles in the droplet and the chemical reaction between the generated fine particles and the surface of the glass can be assumed as the chemical mechanism of the formation of ion deposits.

Table 2 shows the presence and absence of ion deposits on various surfaces. Ion deposits were formed on glass surfaces and no ion deposits were formed on hard-coat film, non-hard-coat film and rigid hard-coat film. Since the surface of glass contains much silicon, it was considered that the ion deposit was a substance formed by a chemical bond with the silicon.

From the experimental results of the formation of ion deposits, ion deposits were significantly generated in samples using groundwater and tap water compared with those using rainwater. It was considered that the generation of ion deposits depends on the concentration of ions in water. It is estimated that ion deposits will not be generated if there is no silicon in the water.

Fig. 6 shows the results of laser Raman spectroscopy of glass and glass with ion deposits. A 16.95 ppm silicon ion solution was used to produce ion deposits on the glass surface. Fig. 6 (c) shows the results of laser Raman spectroscopy of silica sand for comparison. From the results of laser Raman spectroscopy, SiO₂ peaks were observed at 463 cm\(^{-1}\) in the sample of glass surface with ion deposits.

Fig. 7 shows the results of laser Raman spectroscopy of hard-coat film, non-hard-coat film and rigid hard-coat film on which no ion deposits were formed. No SiO₂ peak was observed in the samples of these three types of automotive glass film. From the results of laser Raman spectroscopy, the composition of SiO₂ in the ion deposits was clarified. Since the samples with no ion deposits did not contain silicon, it was considered that the adhesive surface did not react with silicon ions in water.

Fig. 8 shows the formation mechanism of ion deposits on a glass surface \(^{(9)}\). When glass surface was used as a coating surface, it was considered that the adhesive interface of ion deposits is a chemical bond with silicon, which is the main component of glass and silicon ions in water. The binding energy of silicon and oxygen is 128 kcal mol \(^{-1}\), which is much larger than that of the silicon–silicon single bond (53.1 kcal mol \(^{-1}\)) \(^{(9)}\). Hence, the ionic bond between silicon and oxygen can be assumed as a selective one.

Fig. 9 shows the formation mechanism of ion deposit on the surface of automotive glass films \(^{(9)}\). When automotive glass film was used as a coating surface, the silicon ions in water did not bond with the surface.
Table 2 Formation of ion deposits on various surfaces.

| Coating surface       | Presence or absence of ion deposits on coating surface |
|-----------------------|-------------------------------------------------------|
|                       | Ground water  | Tap water | Rain water |
| Glass                 | ✓            | ✓         | ✓          |
| Hard-coat film        | ×            | ×         | ×          |
| Non-hard-coat film    | ×            | ×         | ×          |
| Rigid hard-coat film  | ×            | ×         | ×          |

Fig. 6 Results of laser Raman spectroscopy of (a) glass, (b) glass with ion deposits and (c) silica sand.

Fig. 7 Results of laser Raman spectroscopy of (a) hard-coat film, (b) non-hard-coat film and (c) rigid hard-coat film.
3.3. Formation of Ion Deposits on Metal Surface

Table 3 shows the experimental conditions of the production of ion deposits on the surface of aluminium.

| Coating surface | Aluminium |
|-----------------|-----------|
| **Solution**   |           |
| Type           | 0.57–16.95 ppm Si ion solution |
| Pipetting amount | 10 µL   |
| Number of times | 5       |
| Evaporation temperature | 313 K |

Fig. 10 shows SEM and SEM-EDX images (distribution of Si concentration) of ion deposit on the surface of aluminium. The contour of the ion deposit, indicated by red arrows, formed in a ring shape, as shown in Fig. 10 (a). The formation of ion deposit on the aluminium (metal) surface was similar to that on the glass surface. It can be assumed that ion deposit is formed on the metal surface.

Fig. 11 shows the results of laser Raman spectroscopy of surfaces of aluminium and aluminium with ion deposit on its surface. A 16.95 ppm silicon ion solution was used to produce the ion deposits on those samples. The SiO2 peaks were observed at 463 cm⁻¹ in the sample of aluminium surface with ion deposit. Similar with the case of using glass as a coating surface, the formation of ion deposit occurred even when metal was used as a coating surface.

Fig. 11 Results of laser Raman spectroscopy of (a) aluminium and (b) aluminium with ion deposit.
Fig. 12 shows the formation mechanism of ion deposits on the aluminium surface (9). The adhesion interface of ion deposits was considered as a chemical bond between the aluminium and silicon ions in water when the aluminium was used as a coating surface. Because of the cationic property of aluminium, an easy reaction with the anionic substance was considered.

![Formation mechanism of ion deposits on aluminium surface](image)

**Fig. 12 Formation mechanism of ion deposits on aluminium surface.**

### 3.4. Removal of Ion Deposits with Low Concentration of Hydrofluoric Acid

A glass slide with dimensions of 20 × 15 mm² and 1 mm thickness was used as a substrate. Table 4 shows the experimental conditions of the production of ion deposits and their removal (cleaning) using hydrofluoric acid (49.5–50.5%; Kanto Chemical). For this process, 1 mL of 23.15 ppm silicon ion solution was pipetted onto the surface of the glass substrate. The solution-coated samples were dried at 313 K with a hot plate until the droplets were completely evaporated. The pipetting and drying (evaporation) processes were repeated 25 times. Then, ultrasonic cleaning was performed in distilled water to remove water-soluble substances and the production of ion deposits was completed. In addition, the mass of the sample was measured with an electronic balance.

For removal of ion deposits, 1 mL of prepared 0.1–5.0% hydrofluoric acid was applied with a cotton swab to the prepared ion deposit sample. The mass of the cleaned sample was measured with an electronic balance, hence the mass of the removed ion deposit and glass could be calculated.

**Table 4 Experimental conditions of production and removal of ion deposits.**

| Coating surface | Glass |
|-----------------|-------|
| Solution Type   | 23.15 ppm Si ion solution |
| Pipetting amount| 1.0 mL |
| Number of times | 25 |
| Evaporation temperature | 313 K |
| Hydrofluoric acid Concentration | 0.1–0.5% |
| Pipetting amount | 1.0 mL |

Fig. 13 shows the dependence of removal weight on the concentration of hydrofluoric acid. As shown in Fig. 13, about 1 mg of ion deposit and glass was removed by cleaning with 0.5% hydrofluoric acid. Since the amount of removed ion deposit depends on the concentration of hydrofluoric acid, it was considered that repeated cleaning with less than 5000 ppm hydrofluoric acid is an efficient cleaning method for ion deposits.

**Fig. 13 Dependence of removal weight on concentration of hydrofluoric acid.**

**Fig. 14 Mechanism of removal of ion deposits by hydrofluoric acid.**

### 4. Conclusion

The production of ion deposits was performed on glass and various automotive glass films and automotive coating agents. Ion deposits containing silicon formed in a ring shape on the coating surface by the evaporation of water droplets. From the results of laser Raman spectroscopy, the composition of SiO₂ in the ion deposits was revealed. The adhesion interface between the ion deposits and the coating surface was considered to be a chemical bond between the silicon ions in water and the coating surface.

Since ion deposits formed not only on the glass surface but also on the car body and metal parts, they were also produced on the metal surfaces. Ion deposits formed on the metal surfaces, similar to the case of using glass surface and coating surface containing silicon. The chemical bond between the silicon ions in water and the metals of coating surfaces was considered to be one of the reasons for ion deposits to form on the metal surfaces.

The removal of ion deposits using various concentrations of hydrofluoric acid was explored as a cleaning method. The removed amount of ion deposit depended on the concentration of hydrofluoric acid, and about 1 mg of ion deposit was removed by using 0.5% hydrofluoric acid. Repeated cleaning with 0.5% or less of hydrofluoric acid is an efficient method for removal of ion deposits.
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