Laboratory test method for dirt pickup resistance and stain removal

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Abstract. The pollution characteristics of current atmospheric particulates was summarized in the present investigation. The composition and proportion of the pollution sources used for dirt pickup resistance and stain removal test were adjusted, and the pollution sources used for new type dirt pickup resistance and stain removal test produced. In addition, a new dirt pickup method was adopted, and a set of new type laboratory dirt pickup resistance and stain removal tests developed by taking comprehensive consideration of the existing state and dirt pickup mode of actual atmospheric particulates. It verifies the rationality, feasibility and effectiveness of new test methods for dirt pickup resistance and stain removal based on the contrast test over the new and old test methods.

Keywords: atmospheric particulates, dirt pickup resistance, pollution source, test method

1. Introduction

Dirt pickup resistance and stain removal are one of the important indicators for evaluating the performance of coated metal plates. In the current test method for dirt pickup resistance and stain removal, the ash which is prepared mainly with graphite powder is adopted as the pollution source, and is brushed on the film test plate, and then the test plate is washed with water in uniform flow under the specified water pressure. In practical operation, the brushing method will cause uneven film layer due to human factors, thus the test result may be affected; in addition, the brushing method is inconsistent with the actual dust fall effect.

At present, the urban atmospheric pollution is becoming increasingly serious; and with the increase of motor vehicle population, motor vehicle exhaust pollution increases greatly. In many large and medium-sized cities, urban atmospheric environment pollution caused by motor vehicle exhaust emission has exceeded 60%, which shows that motor vehicle pollution has become the main source of atmospheric pollution. The organic pollution caused by motor vehicle exhaust emission is predominant and organic matter has become one of most primary components of atmospheric particulates. The pollutants used in the current test methods for dirt pickup resistance and stain removal do not involve any organic matter, thus this paper studies the preparation of new pollutant which better meets the composition of actual atmospheric particulates.

In dirt pickup resistance and stain removal test, the composition and proportion of pollution sources used are the key factors determining the rationality of test method for dirt pickup resistance and stain removal, and meanwhile, the dirt pickup mode determines the feasibility of such test method, a rational and feasible artificial accelerated test method for dirt pickup resistance and stain removal is the final object of this study. This paper carries out a series of studies on how to make the results of
laboratory artificial accelerated test be more approximate to those of outdoor exposure test and how to make the test results truly and rationally reflect the dirt pickup resistance and stain removal of film.

2. Method and theory

Atmospheric particulates belong to a kind of complex mixture and a group composed of the solid and liquid particulates of different particle sizes. The size and distribution mode of atmospheric particulates are closely related to their properties and their influence on environment. Therefore, the study on pollution characteristics of atmospheric particulates must take the size composition, particle size and distribution into account [1-2].

Based on the current findings of investigations on atmospheric particulates, PM10 concentration in atmospheric environment exceeds 80%. In addition, according to "Greenfield Window" theory, the particulates with particle size between 0.1μm and 10μm are hard to be effectively eliminated during the formation of rain from atmospheric water vapor, i.e., the particulates within this particle size range are the main components of atmospheric particulates [3-5].

According to the source apportionment of atmospheric particulates by environmentalists in China, fugitive dust sources are the important source of PM10 in most areas of China, therein the proportion of soil dust, road dust, cement and construction dust in PM10 may be as high as 80%. Secondly, the proportion of organic matter and carbon black caused by industrial emission and vehicle exhaust emission also reaches 20%~40% [6]. These components basically are the sources of main components of atmospheric particulates.

According to statistics, the motor vehicle population in Beijing in 2012 is about 5,200,000, which is a huge amount. According to the analytical prediction of experts, around 2020, the motor vehicle population in China will reach 200,000,000; the annual average growth rate of vehicle population in Shanghai in recent 10 years is also above 10%. The continuous growth of urban motor vehicle population brings great convenience for the life of residents, but also increases the environmental load. Based on the findings from studies on atmospheric particulates, the pollution source from motor vehicle exhaust emission is the main component of PM2.5 in Beijing. According to statistics, only in 2013, the proportion of pollution caused by motor vehicle exhaust emission in PM2.5 increased by approximately 10% [7], the contribution rate of motor vehicle exhaust emission to hydrocarbon compounds in atmospheric pollution reached 73.5%, this figure in the central area of Shanghai also reached 96%, and similar situation also happened in Tianjin, Chongqing, Guangzhou, etc. [8].

In the source apportionment of atmospheric pollution in Beijing, the State Environmental Protection Administration of China analyzes that, from the point of view of composition, the organic pollutants account for 26% of PM2.5 (proportion of PM2.5 in PM10 is about 70%); from the point of view of sources, 64%~72% of atmospheric pollution is locally caused in Beijing. While among the local sources, the proportion of motor vehicle emission (accounting for 31.1%) and coal burning (accounting for 22.4%) exceeds 50%; and the correlational studies show that the contribution rate of volatile organic compounds (VOCS) exhausted by motor vehicles to the atmospheric pollution in urban area of Shanghai exceeds 65% [9]. Cui Mingming et al [10], have analyzed the atmospheric inhalable particulate matter (PM10) sample nearby the district of Guangzhou City and concluded that the mass concentration of organic matter in PM10 was 24%~32%.

The pollution source used for dirt pickup resistance and stain removal test of exterior wall coating shall follow certain selection principles:

1) As pollutants vary from area to area, the selected pollution source shall be with certain representativeness and universal applicability;
2) In order to ensure personal safety of experimenters, the prepared pollution source shall be nontoxic and nonhazardous;
3) This pollution source is used for commenting the dirt pickup resistance and stain removal performance of exterior wall coating, and it shall be with good reproducibility and stability in order to make the test results be more convincing.
As for dirt pickup resistance test and stain removal of external wall coating, China adopts GB/T 9780-2013 Test Method for Dirt Pickup Resistance and Stain Removal of Film of Architectural Coatings and Paint, and in this test, the standard ash sample prepared mainly with graphite powder is adopted as the pollution source [11]. The composition of current atmospheric particulates becomes complicated increasingly. As reported by the Ministry of Environmental Protection, the contribution rate of motor vehicle exhaust emission to atmospheric environment pollution reaches 50~60% in most large and medium-sized cities in China, and this figure may be much higher in some cities with rapid development. This shows that the motor vehicle emission pollution has already become the main source of part of atmospheric pollution, organic pollution is serious and organic matter has become one of the most primary components of atmospheric particulates.

Upon study, it is found that saturated hydrocarbon in motor vehicle exhaust mainly consists of n-alkanes, and n-alkanes containing less than 25 carbon atoms is mainly generated from such human activities as combustion of fossil fuel and coal, and the alkane containing more than 26 carbon atoms is from emission of biological source. In various cities, the distribution range of n-alkanes is approximately C10–C35, and the main carbon peak basically is C22–C27. Therefore, a kind of saturated hydrocarbon, i.e. n-Tetracosane (C24), is selected as the organic matter added in the pollution source used for dirt pickup resistance and stain removal test.

Upon comprehensive analysis as well as reference to the pollution sources used in current dirt pickup resistance and stain removal tests at home and abroad, the composition of the pollutant sources in laboratory dirt pickup resistance and stain removal test method is finally selected: loess dust (loess in Shaanxi) - the representative material of fugitive dust sources, n-Tetracosane - the representative material of organic matter, and carbon black.

There into, loess dust is the standard sample simulating the atmospheric dust, while n-Tetracosane and carbon black are provided by the product supply department. Fugitive dust sources are the important source of PM10 in most areas of China, and the proportion of dust in PM10 may be as high as 80%; secondly, the content of organic matters generated from industrial emission and vehicle exhaust emission also reaches 20%~30%, and the ratio of organic carbon to inorganic carbon is about 3 [12]. Reference to current dirt pickup resistance tests: the proportion of No.8 ash in pollutant of Japan Kansai Paint Co., Ltd. is 70%, that of carbon black is 17%; during simulation of atmospheric dust, Germany Sto Ges.m.b.H. determines the proportion of ash and carbon black in dust as 85% and 15% respectively. According to the aforesaid data, the proportional range of three components of the new pollution source are temporarily taken as 70%~80% for loess dust, 20%~30% for n-Tetracosane and 5% and 15% for carbon black.

As for the three components of pollution source powder, in addition to following the aforesaid proportion of mixture, appropriate mixing method also shall be selected. In this study, three kinds of powder are mixed in liquid state and solid state respectively, and comparison is carried out based on the color and state of mixture; thereinto, mixing in solid powder state improves the mixing uniformity and also meets existence of actual atmospheric particulates in nature; meanwhile, with consideration of simulating the actual pollution mode of atmospheric particulates - dust fall, the pollution source powder is hereby sprayed, and the proportion of these three pollution sources are finally determined, as shown in table 1.

| Component       | Loess dust | n-Tetracosane | Carbon black |
|-----------------|------------|---------------|--------------|
| Proportion      | 75%        | 20%           | 5%           |

In this dirt pickup resistance and stain removal test, both loess dust and carbon black used are standard materials, of which the particle diameter is less than 100μm, and only n-Tetracosane has nonuniform particle size and is flaky. Dry powder mixing method is adopted and organic solvent cannot be added, thus n-Tetracosane (melting point: about 55℃) is heated to melt on heating plate at about 55℃, then is added with loess dust and carbon black and stirred sufficiently by manpower so as
to mix the three components uniformly, and the mixture is sufficiently ground in mortar to obtain the pollution source powder.

Table 2. Test Results of Loss on Ignition.

| Batch No. | No. | Weight of sample before ignition(g) | Weight of sample after ignition(g) | Loss on ignition(%) |
|-----------|-----|-------------------------------------|------------------------------------|-------------------|
| First batch | 1   | 1.0633                              | 0.7123                             | 32.07             |
|           | 2   | 1.0192                              | 0.6997                             | 31.35             |
|           | 3   | 1.0324                              | 0.6937                             | 32.45             |
|           | 1   | 1.0536                              | 0.7199                             | 31.67             |
| Second batch | 2   | 1.0603                              | 0.7258                             | 31.55             |
|           | 3   | 1.0507                              | 0.7073                             | 32.68             |
|           | 1   | 1.0464                              | 0.7192                             | 31.27             |
| Third batch | 2   | 1.0250                              | 0.6959                             | 32.11             |
|           | 3   | 1.0790                              | 0.7328                             | 32.09             |
|           | 1   | 1.0761                              | 0.7331                             | 31.87             |
| Fourth batch | 2   | 1.0304                              | 0.7003                             | 32.04             |
|           | 3   | 1.0756                              | 0.7347                             | 31.69             |
|           | 1   | 1.0268                              | 0.6921                             | 32.59             |
| Fifth batch | 2   | 1.0341                              | 0.7008                             | 32.23             |
|           | 3   | 1.0683                              | 0.7266                             | 31.99             |

Pollution source powder is stirred, ground and mixed manually, thus the generally applicable loss on ignition test requiring relatively simple operation is carried out to inspect the mixing uniformity of pollutant. Five groups of pollution sources prepared at different time are taken, and three samples are randomly taken from each group for the loss on ignition test. The test results are as shown in table 2-5.

The test method and data statistical method for uniformity are as follows:

As for the test results, variance analysis method is adopted to calculate the five groups of data, with group consisting of repeated results from three independent measurements, and the test results of uniformity of pollutant are as shown in table 3.

Table 3. Result of Uniformity.

| Sample No. | Uniformity | Result 1 | Result 2 | Result 3 |
|------------|------------|----------|----------|----------|
| 1          | 32.07      | 31.35    | 32.45    |
| 2          | 31.67      | 31.55    | 32.68    |
| 3          | 31.27      | 32.11    | 32.09    |
| 4          | 31.87      | 32.04    | 31.69    |
| 5          | 32.59      | 32.23    | 31.99    |
| \(\bar{X}\) | 31.98      |          |          |
| \(SS_{within}\) | 0.6943 |          |          |
| \(SS_{among}\)  | 0.3665    |          |          |
| \(MS_{within}\)  | 0.0916    |          |          |
| \(MS_{among}\)   | 0.0694    |          |          |
| \(F\)            | 0.76      |          |          |
| \(F_{0.05(19,20)}\) | 2.14  |          |          |

Conclusion: according to the test results, F value of loss on ignition is 0.76, which is less than the critical value \(F_{0.05(19, 20)}=2.14\), and this shows that the uniformity of new pollutant meets the relevant requirements.

Upon particle size test of \(n\)-Tetracosane, loess dust and carbon black, three materials are mixed with the aforesaid method to prepare the pollution source used for new type dirt pickup resistance and
stain removal test. It is found that the uniformity of this mixture meets the requirements upon uniformity test.

3. Material and experiment

The pollution source powder prepared with aforesaid method shall be sprayed with appropriate container. Simple spraying unit manufactured in laboratory: the top surface is screen mesh in hole diameter of 0.1mm, the whole container body is made of stainless steel, and pollution source powder is let "fall" onto the film test plate by this unit to simulate the actual dirt pickup mode of atmospheric particulates, i.e., dust fall.

Samples: new pollution source, three pieces of 70mm*150mm aluminium veneers with fluorocarbon film, with polyester film and with powder film respectively.

Instruments: electronic balance; self-prepared powder spraying unit; magnetic stirrer; dirt pickup-resistant washing device; electro-thermostatic blast oven; colorimeter.

Standard test conditions: (23±2) °C; relative humidity of (50±5)%.

The investigation shows that the pollution process of atmospheric particulates in Beijing presents obvious periodicity, with typical period of 4~10 days and average period of 5~7 days, and such a periodicity is essentially determined by the periodical typical cycle synoptic systems. In consideration of the influence brought by the periodicity of pollution as well as by reference to current dirt pickup resistance and stain removal test methods, this test adopts 5 dirt pickup-flushing cycles [13].

Test procedure: weigh 1g of pollutant powder into self-made powder spraying unit. Take the sample plate and test the initial reflection coefficient of this film test plate at three positions, i.e., upper, middle and lower parts, with colorimeter, and calculate their average value and record it as \( L_1 \). Spray pollutant powder with the self-made spraying unit to let the power uniformly "fall" down to the test plate, place the test plate covered with pollutant into a (60±2) °C drying oven and keep it here for 2h, then take it out and keep it still for 2h under standard test conditions, then place the test plate on test plate holder of washing device and wash it by making reference to GB/T 9780-2013 Test Method for Dirt Pickup Resistance and Stain Removal of Film of Architectural Coatings and Paint. Carry out this spraying-flushing process for five cycles in total, wait till the moisture on surface of test plate is evaporated, then test reflection coefficients at three positions (at upper, middle and lower part) of test plate again, calculate their average value and record it as \( L_2 \).

Result is calculated according to the following formula:

\[
X = \left( \frac{L_1 - L_2}{L_1} \right) \times 100\%
\]

Where,
- \( X \) - the decrease scale of the reflection coefficient of film;
- \( L_1 \) - the initial average reflection coefficient of film;
- \( L_2 \) - the average reflection coefficient of film after dirt pickup test.

As for the films of three kinds of materials, i.e., fluorocarbon, polyester and powder, the arithmetic mean value of three test plates is taken, and the result is retained with two significant figures.

3.1. Comparison with GB/T 9780-2013 Test Method for Dirt Pickup Resistance and Stain Removal of Film of Architectural Coatings and Paint

The test is divided into two groups. Group I is dirt pickup resistance and stain removal test in accordance with GB/T 9780-2013 Test Method for Dirt Pickup Resistance and Stain Removal of Film of Architectural Coatings and Paint, and Group II is dirt pickup resistance and stain removal test with the aforesaid new type test method.

The test results are as shown in table 4.
Table 4. Dirt Pick Resistance and Stain Removal of Film.

| Film type | Group I Decrease scale of reflection coefficient after dirt pickup test $X$ | Average | Group II Decrease scale of reflection coefficient after dirt pickup test $X$ | Average |
|-----------|-------------------------------------------------|---------|-------------------------------------------------|---------|
| Fluorocarbon | 0.42 | 0.47 | 5.99 | 6.12 |
| Powder | 1.33 | 1.26 | 13.08 | 16.05 |
| Polyester | 0.24 | 0.225 | 10.63 | 10.92 |

The two groups of test results show that the metal plate with fluorocarbon film has the best dirt pickup resistance and stain removal, followed by the metal plate with polyester film, with the metal plate with powder film ranked last, thus the law is consistent and conforms to actual situation. Upon comparison of two groups of test results, the average value of decrease scale of reflection coefficient in Group I tests is less than 2, and the contrast effect of film test plates is not obvious; the results of Group II tests show certain gradient interval and are convenient for distinguishing the dirt pickup resistance and stain removal of different film test plates.

3.2. Contact angle test
The contact angle test and dirt pickup resistance and stain removal test are carried out respectively with fluorocarbon, polyester and powder film test plates, and the contact angle is as shown in table 5.

Table 5. Test Result of Contact Angle.

| Film type | Contact angle $\theta$ | Average value of contact angle | Decrease scale of reflection coefficient (%) |
|-----------|------------------------|-------------------------------|---------------------------------------------|
| Fluorocarbon | 78.50° | 74.10° | 73.25° | 75.28° | 6.87 |
| Polyester | 76.85° | 74.96° | 72.24° | 74.68° | 10.31 |
| Powder | 71.99° | 71.33° | 71.92° | 71.75° | 16.93 |

4. Results and discussion
Based on the research of atmospheric particulates, a new kind of pollution sources used in powder contamination resistance test was born, adjust the corresponding way at the same time, formed a new laboratory artificial accelerated fouling resistance test method.

Through the research of atmospheric particulates, found that the increase of motor vehicle ownership makes the motor vehicle emission pollution become the major source of atmospheric pollution, organic pollution is serious, and the organic matter becomes the important component of atmospheric pollution. And then through the research of vehicle exhaust emissions of organic ingredients found that the important part of the corresponding normal alkanes was developed, according to the survey, the corresponding normal alkanes was finally selected the 24 silane as a new pollution source is the representation of the organic material, at the same time reference fouling resistance test method at home and abroad, it finally determine the composition of pollution sources, namely the loess dust (shaanxi loess), soot, and organic compounds are twenty-four alkanes. Through the component proportion of debugging, and ultimately determine the composition proportion respectively: loess dust (75%), carbon black (5%), is 24 (20%) of three kinds of pollutants in accordance with the proportion mixing produced new contamination resistant test powder with sources. Due to the accuracy and simplicity, loss on ignition used to test the uniformity of the new dust, and the experimental results F value is 0.76, less than the critical value $F_{0.05} (19, 20) = 2.14$, which shows that the new pollution sources is qualified from uniformity.
The atmospheric particulate contamination fallout on the roof and wool space, in order to simulate the atmospheric dust fall, a homemade fallout device was tried to make the new pollution sources "fall" on the coating plate, which formed a new stain resistance test method.

In the first experiment, two groups of test results show that the metal plate with fluorocarbon film has the best dirt pickup resistance and stain removal, followed by the metal plate with polyester film, with the metal plate with powder film ranked last, thus the law is consistent and conforms to actual situation. Upon comparison of two groups of test results, the average value of decrease scale of reflection coefficient in Group I tests is less than 2, and the contrast effect of film test plates is not obvious; the results of Group II tests show certain gradient interval and are convenient for distinguishing the dirt pickup resistance and stain removal of different film test plates.

The second, which is contact angle test results show that, fluorocarbon contact angle > polyester contact angle > powder contact angle. Based on the aforesaid sticking-wetting theory, the larger the $\theta$ value is, the lower the surface energy of film is, and the better the dirt pickup resistance and stain removal are. This shows that the fluorocarbon film has the best dirt pickup resistance and stain removal, the decrease scale of reflection coefficient of fluorocarbon film is minimum among the results obtained with new type method for dirt pickup resistance and stain removal, i.e. the dirt pickup resistance and stain removal are the best, followed by polyester film, with powder film ranked last, and this is consistent with the test result of contact angle.

5. Conclusion and outlook
Dirt pickup resistance and stain removal are important indicators for evaluating the performance of coated metal plates. The composition and proportion of pollution sources are the key factors determining the rationality of test method for dirt pickup resistance and stain removal, and meanwhile, the dirt pickup mode determines the feasibility of such test method. At present, the increase of motor vehicle population changes the composition of atmospheric pollutants, and the organic pollution becomes serious, while in the current test method for dirt pickup resistance and stain removal, the ash which is prepared mainly with graphite powder is adopted as the pollution source and cannot sufficiently embody the composition features of current atmospheric pollutants; moreover, the dirt pickup mode with contaminating fluid adopted in current test method also has certain difference from the dust fall mode of atmospheric particulates. Therefore, a rational and feasible artificial accelerated laboratory test method for dirt pickup resistance and stain removal should make comprehensive consideration in such aspects as selection of pollution source and determination of dirt pickup mode, so as to be more in line with the actual dirt pickup condition.

As for the new type test method for dirt pickup resistance and stain removal, both the composition of pollution source and the dirt pickup mode are adjusted, but the preparation of pollution source and the dirt pick process are manually carried out, the standard and uniform preparation of pollution source powder requires further improvement, and the self-made dirt pickup unit also requires further standardization; in addition, the new type test method for dirt pickup resistance and stain removal covers verification test over three kinds of usual films only, does not include any comparison with the natural solarization test, and is even lack of universal applicability, thus this new type test method for dirt pickup resistance and stain removal will be further refined and improved in the next research work to form a standard system.

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