ORGANIC COATINGS: Properties and Evaluation

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Introduction

Paints have been part of man's environment for thousands of years. The cave man was probably the first who tested a paint to see if it was dry enough to apply another color when completing his cave paintings.

For centuries paints were used for decorative purposes. Only after the industrial revolution were paints employed for the protection of various substrates. The earliest coatings were used for the protection of iron parts which had a tendency to corrode rapidly, especially near the sea. As the manufacturing and shipping industries grew, other problems of protection developed and new and more effective coatings became available.

In today's highly industrialized society large amounts of paints and paint systems are found ranging from the simple latex-based, water-thinnable wall paint, used in housing, to the multilayered, polymeric, resin coatings used in waste disposal or nuclear generating stations.

All other paints are collectively referred to as coatings and have one thing in common—they are produced against a set of requirements which are commensurate with the performance demanded of the dry paint film, and are applied to the substrate. As an example, an architectural paint is designed to give the interior wall a certain color and provide an aesthetic experience for the viewer. An epoxy-based enamel, used on a mixing tank, is designed to provide a smooth, easily-cleanable surface and to protect the steel members from corrosion. The application and demands are too numerous to mention.

This book provides a comprehensive discussion of the physical properties of coatings, how they are measured, and how these factors are used to evaluate quality, inherent performance, and durability of the coating.

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1.

Adhesion

Before the various methods and instruments which measure adhesion of organic coatings can be evaluated, it is important to understand the fundamentals of measuring adhesion. This property, by definition, is the state in which two surfaces are held together by forces, which may consist of valence attractions or interfacial forces or a combination of both. Interfacial forces could be defined as physical bonds, whereas valence attractions are chemical in nature. The interfacial forces are too small to be measurable by any mechanical device and if they could be measured it would be found that most "adhesive" failures are cohesive failures of the films tested.[1]

1.1 Factors Affecting Adhesion

There are two major factors which affect the adhesion of organic coatings to various substrates and these are:

1. The affinity of the solvent and the resin in the coating for the substrate, or, as the term is used, the wettability of the substrate by the coating
2. The profile or roughness of the substrate.

The first is referred to as the specific adhesion, the second, the mechanical adhesion.

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[1] Corcoran, E. M. *Paint Testing Manual* STP 500, ASTM 1972.

In order for a specific adhesion to be formed there must be an initial interaction between the solvent system and the substrate, followed by an absorption of the polymeric phase onto the substrate. The manner in which this polymeric phase is formed is crucial to the proper bond formation and hence to a good adhesiveness. In most organic coatings, this bond is strictly mechanical and in the process smaller molecules of the solvent are partially replaced by the larger molecules of the polymers (or binders) used in the vehicles of the coatings.

It has been shown that the presence of low molecular weight fractions in the solvents or resin system can form a weak boundary layer which is composed of inherently weak substances at or near the coating substrate interface, that substantially reduce the apparent adhesion.[2] The theory of surface chemistry states that organic materials in the liquid phase should freely wet and adhere to metals and metal oxides, but in some coatings, the weaker constituent may wet out the substrate preferentially.[3].

The cleanliness of the substrate is a major factor for proper adhesion of any organic coatings. The surface must be free from oils, greases, and other foreign, film-forming materials which can reduce the wettability of the substrate. The coating must be applied to oxide-free surfaces (in the case of metallic substrates) since their presence would prevent the formation of any chemical bond between metal and coating, as in the case of metallic primers.

If adhesion is defined as interfacial forces between coating and substrate, then their magnitude cannot be measured by mechanical means. Since adhesion cannot be measured, as such, it is necessary to determine the forces needed for the removal of the coating from its substrate.

Organic coatings are removed by an empirical scratching with a sharp blade, by a mechanically operated knife, by exposure to high-speed vibration, or by high-speed centrifugal force. The amount of force necessary is then measured and a value for adhesion is ascribed to the coating. Another method is to apply a given force, using a definite instrument or device. The resulting delamination, in quantitative terms, is directly proportional to the adhesion of the coating.

1.2 Adhesion Measurements

Adhesion is measured by forces necessary for the coating's removal, under controlled conditions. The wide range of methods of removal and devices have been employed over the years and they can be classified as follows:

1. Knife—the cutting with a sharp edge
2. Scratching or scraping
3. Adhesive joint:
    a) Direct tensile
    b) Shear or torque
    c) Cleavage
    d) Tensile shear
4. Peel
5. Inertia

KNIFE REMOVAL METHODS

A skilled technician can determine the relative adhesiveness of organic coatings by this method. The problem with this method is that quantitative information is not possible to obtain. The test consists of placing a sharp knife blade at an angle of 30–45° to the panel (to which the coating has been applied) and moving the knife through the coating, cutting a ribbon. The cut coating should roll into a continuous concentric ribbon without flaking or without partial adhesion of the coating on the panel. The method has been standardized in FTMS 141 method 6304. The description of the method is too vague and insufficient to enable any two operators to perform this test with the same results.

The knife test was modified and resulted in the *Rossman Chisel Adhesion Test.*[4] In this test a chisel under a definite load is made to bite into the film at a fixed angle. Meanwhile, the panel to which the film has been applied is drawn against the edge of the chisel by means of a spring. The tension of the spring is diminished during the test until the force is insufficient to separate the film from the substrate. The device is shown in Fig. 1.1 but in practice the chisel is a new razor blade and it is so adjusted as to cut a path 1.0-cm wide. The initial force is usually 10 kg and the spring tension varies from 2–10 kg. The true tension curve is recorded on a rotating drum. From the curve obtained the adhesive strength of the coating can be calculated.

A modification of the Rossman chisel is the *New York Club Chisel Adhesion Test.*[5] This device is similar to the Rossman except the tension on the chisel is increased to a point where complete removal of the coating occurs when the device is moved over the coated substrate. The force of the spring is read directly on a calibrated scale.

A scientific refinement of the old-fashioned knife test was introduced in 1944 and later adapted by ASTM as method D 2197 entitled, *Adhesion*

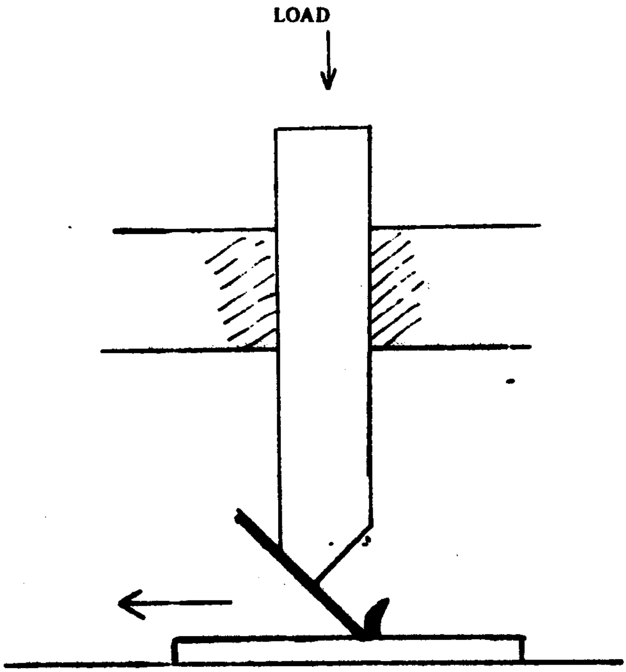

Fig. 1.1 Rossman Chisel Adhesion Test.

of Organic Coating by Parallel Groove Adhesion and the federal government in FTMS 141 Method 6302.1. The adhesion is evaluated in terms of the closeness with which parallel grooves can be cut into the coating before the intervening film is pushed off or lifted from its substrate. The device consists of a movable stage on which the test panel is firmly attached, a 60-degree, conical, diamond-point, cutting tool with an 85 degree axis to the test surface in the cutting direction, and a beam of sliding weights, capable of applying a load of up to 1000 g to the cutting point. The platform holding the panel can be moved by means of a calibrated micro-screw in the direction perpendicular to the cut to produce a series of parallel grooves with any spacing between them at increments of 1.0 mil (0.001 in.).

The microknife adhesion is calculated from the following equation:

$$A = 100D/L_A^{1/2} = D/C$$

$$C = L_A^{1/2}/10$$

where

L_A is the minimum beam load.

Using the load, L_A, and starting with a spacing of 20 mils between the grooves until a distance (D) is reached at which the coating between the grooves is lifted or torn from the substrate. For coatings of similar thickness and composition the apparent adhesion is a function of the load on the stylus and distance between the grooves at failure of the coating to remain attached to the substrate.

The other devices which are based on the same principle are: the *Graham-Linton Edge Adhesion Test*, outlined in military specification MIL-P-19834; the *DuPont Sharp Tool Adhesion Test*, employing the DuPont scratchmaster; and the *Hesiometer*, developed by the staff of Union Carbide.[6]

SCRATCHING OR SCRAPING METHODS

Cross-Cut Adhesion. In this test parallel cuts are made through the coating in one direction and another series of cuts are made perpendicularly to the first cuts to form a series of small squares, originally one hundred of them, 1/32 in. in size. The previously described microknife is used for the scoring of the coating. The number of squares from which the coating peels or fails to adhere gives a quantiative value to its adhesive power.

Too many variables enter into this test and its accuracy and reproducibility remain questionable. Film thickness, depth of the cut, width of the cut, and the angle of the cutting edge all contribute to the inaccuracy of this method. All subsequent methods, described below, are designed to eliminate these difficulties.

One of the tests which gained some popularity is described in ASTM D 3002, D 3359, and DIN 5351 and consists of a series of parallel cutting wheels, spaced 1.0 mm apart, which cut through the coating making six lines, a second cut is made perpendicularly to the first, thus creating 25 squares of 1.0 mm each. An adhesive tape is applied to the cross cuts, the tape is rolled in place to assure good adhesion, and is then removed with a force perpendicular to the coated substrate. The number of squares from the coating that is removed gives the numerical value of its adhesiveness.

Automatic Scrape-Adhesion Test. In this test developed by Bell Labs, the coating applied to a metal substrate moves under a weighted loop of wire, while at the same time the load on the loop is continuously increased by moving a weight along a beam to which the loop is attached. When the coating is completely removed and there is a loop-to-metal substrate contact, a relay trips the mechanism and the load at that point can be determined. This method is unique since there is a continuous increase in the force on the scraping point (loop).

Balance Beam Scrape Adhesion Test.[7] Here, employing the same principle, the scraping tool is a stylus made of a chrome-steel drill rod, having a diameter of 0.0625 in., which is bent into a loop with an outer radius of 0.128 in. During the test the coating is moved horizontally under the weighted loop, using 50 g incremental weights until the coating breaks. Each time the weight is increased a new scrape of the coating is made. Examination of the test shows that the loop actually plows through the coating. The weight necessary to delaminate the coating is its adhesiveness.

Scrape Adhesion Tester. This was developed by Bell Labs[8] and consists of a spring load which protrudes through the bottom of a small housing so that it is slightly below the carriage wheels. The load on the loop can be varied by changing the spring tension from 0–10 kg. It is small and can be carried in a pocket. It is used mostly for rough estimates of adhesion under field conditions—for go and no-tests, meaning that a predetermined weight is set and the coating tested for adhesion or adhesion failure.

The Hoffman Scratch Test. This test was originally included in the Federal Test Method Standard (FTMS) No. 141 as Method 6303, but has been eliminated from the latest revisions of the standard. In this test,[9] a small, four-wheeled carriage, having a weighted lever on one side equipped with a sharp-edged steel cylinder set at a 45-degree angle to the plane of the sample, is drawn across the coated substrate. The cylinder is attached to the lever arm and the load is varied by changing the position of the weight on the notched lever arm. This device has been successfully used for the determination of adhesion, scratch or mar resistance, and relative hardness of organic coatings.

Angular Scribe-Stripping Technique. This is sometimes referred to as the Tooke test and in its modified form, the paint inspection gauge.[10] It is portable and hand-operated. It consists of a tungsten-carbide cutting tip and a 50-power microscope fitted with a calibrated reticle. The tip is used to cut into the coating to the substrate at a low angle to the horizontal plane. The width of the exposed 'interface' is measured with the calibrated scope. The reference number is then calculated from the formula:

$$A.N. = \frac{\text{thickness (mils)}}{\text{width of strip (mils)}} \times 10 \qquad (1\text{-}1)$$

$$A.N. = \text{adherence number} \qquad (1\text{-}2)$$

ADHESIVE JOINT METHODS

Direct Tensile. The ASTM Method D 879 entitled, *Tensile Properties of Adhesives*, was adapted for coating adhesiveness and involved using two plugs of base metal (usually steel) with the coating under test between them. After proper curing the plugs are pulled apart in a tension tester. The method has been criticized by its users as having many disadvantages, e.g., the inability to distinguish between cohesive and adhesive failure by the coating, and the problem of poor reproducibility.

Shear or Torque. The *Rossmann Tensile Method* is based on the same principle.[11] The two surfaces used are usually 2.5 mm in diameter and are either metal rivets or wooden dowels. The coating is applied by any suitable means to one end. The ends of the two cylinders are then clamped together, overlapping for a distance of 10 mm. The assembly is permitted to dry for a given period. The pieces are pulled apart by a spring-loaded dynamometer or low-range tensile machine. The load required is under 3.0 kg.

After separation the width of the broken area can be measured under 20X magnifications and the adhesion calculated:

$$\text{Adhesion} = \text{load/area} \qquad (1\text{-}3)$$

If the adhesion is unusually high the pieces can be separated by lever action. In this case, the adhesion is considered to be concentrated at P, midway between the ends of the overlap, and the adhesion is calculated as:

$$\text{Adhesion} = (\text{load} \times B) / (\text{area} \times A)$$

where the mechanical advantage is B/A.

Cleavage. The *Pencil Scratch Hardness Test* has been used to determine adhesion.[12] The difference is that the hardness of the pencil that will just scratch the coating off the substrate is considered as its adhesion number (see hardness, pencil scratch).

In the early 1930's a method based on direct tensile was devised which treated the applied coating as an adhesive. The method was erratic and could not be reproduced. Essentially the wet paint film was used as an adhesive between two identical plates (usually steel). After the paint film dried and was fully cured, the force necessary to pull the plates apart was designated as its adhesive strength.

About ten years later the ASTM method for tensile adhesion (D 879) used for adhesives was tried for coating adhesion. The method consisted of applying the coating to two plugs of base metal and pulling them apart in a tensile tester.[13] The author of this method noted that the method had the disadvantage of treating the coating as an adhesive and failing to distinguish effectively between cohesion and adhesion. The method also exhibited a high degree of variability and failed to yield reproducible results.

The *General Electric Plug Method* gained some popularity during 1950–60. In this method the coating is applied to a small plate which has been ground flat. After the coating has cured or dried, a cone-shaped member is bonded to the coating. A precise alignment is obtained by the use of a special jig. The members are then pulled apart in a tensile machine. There were many variations of this method in which only one, or both surfaces were covered with the coating, none of which gave reproducible results and the method was abandoned by the industry.

Tensile Shear. In the *Tensile Shear Test*, which was developed by the New York Production Club and widely used[14] the adhesion of the coating was measured by tensile shear instead of direct pull. The selected metal panel is coated with the material under test, dried, and permitted to cure. Prior to testing the panel is cut with 1.0 in. X 3.0 in. strips. A strip of wood (2½ in. X 7 in.) is placed in the middle of a 12 in. X 12 in. metal panel. A strip of Bakelite plyboard BC 11297 (1 in. X 7 in.) is laid on the wood strip along one edge. Next the varnished faces of the test specimen are laid on the plyboard to produce 1 in.^{2} overlaps. A second 12 in. X 12 in. metal panel is laid on top and the entire assembly is placed in a press. A pressure of 300 psi at a temperature of 280 F is applied for 5 min. The wood strip is then cut between the metal test specimens. In this way a test specimen is prepared, in which the varnished metal strips and the wood strips are cemented together and overlap over an area of 1 in.[2] This specimen is placed in a tensile machine and the load required to break is called the adhesion value. Adhesion values obtained on a large number of coatings during a round-robin test program ranged from 100 psi to 600 psi. It was found that many variables affected the adhesion value. Some of these were the temperature of the cure and the thickness of the coating when in excess of 3.0 mils.

PEEL METHOD

The final test used for the determination of adhesion that is discussed here is the *Peel Test*. In this test[15] the coating is applied to a metal panel and while still tacky a piece of silk cloth is pressed into the soft film. After the coating has fully cured, the panel is cut into 1.0-in. wide strips, a portion of the cloth removed and the entire assembly is placed into a tensile machine. The metal is held in the stationary part of the machine and the cloth is pulled at a 180 degree angle slowly from the coated portion of the panel. This method gives good reproducible results and can differentiate between lacquers to which various resins and plasticizers have been added. This method is also capable of determining intercoat adhesion of two or more coats of the same or different material. The method has been widely used for the determination of adhesion of lacquers and nitrocellulose dopes.

INERTIA METHOD

With the advent of more sophisticated technology, a different method for evaluating the adhesion of coatings has been used. The *Ultracentrifuge Adhesion Test* was developed as a research tool and consists of measuring the speed of an electromagnetic centrifuge at which the forces will throw off a spot of coating which has been applied to the rotor. The coating is applied to the rotor at 1/8-in. diameter and a thickness of 3.0 mils. The speed of the rotor is measured by light reflected from it as it spins. The variation of the light which is reflected from the painted and unpainted portion of the rotor are visible as a pattern on an oscilloscope. When the paint is removed by the centrifugal forces, the pattern changes. The speed can be calculated. Speeds up to 2×10^6 *rpm* have been obtained which were calculated to a force equal to 24×10^6 greater than gravity.[16]

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2.

Flexibility

The term flexibility is used frequently in the paint industry, despite the fact that no exact definition exists to describe this physical property of coatings. Webster defines it as the capability of being bent, turned, or twisted without being broken and with or without returning to its former shape. In the *Glossary for Protective Coatings*, the following definition is found:[1]

> Paint and varnish films must have sufficient elasticity so that they will not split or crack following the shrinkage of the film or movement of the substrate due to weather or service conditions.

It can be readily seen from the various uses of coatings that the requirements for their flexibility varies greatly. Consider an engine enamel applied to a heavy cast iron base against a similar coating applied to a flexible substrate, such as an automotive fender. The requirements for their relative flexibility are very different.

The main reason for the absence of an authoritative definition for flexibility is the number of variables affecting it. The flexibility depends not only on the elasticity of the applied film, but also on the adhesion of the film to the substrate. It has been shown that well-adhering films have better flexibility than those which adhere poorly. Most flexibility tests emphasize the ability of the film to resist cracking and/or chipping under conditions usually more severe than encountered under actual use conditions. The exposure to sunlight produces some photochemical changes in most polymers due to the influence of ultraviolet radiation. This change usually affects the elasticity and hence the flexibility of coatings. Tests performed on artificially aged and weathered panels are gaining popularity especially on coatings used for the protection of outdoor objects. Comparisons of the flexibilities before and after these exposures give some indication of the coatings' weather resistance and durability in service. Well-founded projections about serviceability can be made.

There are three basic external factors which affect flexibility of any coating.

1. Humidity. Some coatings readily absorb moisture from the air, while others require prolonged periods to achieve an equilibrium with the relative humidity concentrations of the ambient air. It is important that the test panel is maintained in a controlled atmosphere for at least 24 h prior to the test and that the test condition be strictly adhered to. The relative humidity of the test chamber should be 50 ± 5%.

2. Temperature. The flexibility of most coatings is affected by temperature, especially the thermoplastic coatings. They have a transition temperature, below which they exhibit a certain amount of inherent brittleness which increases with the decrease in temperature. On the other hand, in temperatures above this transition temperature they are tough, becoming soft and viscous with an increase in temperature. The standard temperature at which most flexibility tests are conducted is 25 ± 1 C. Lower temperatures are also used and are usually specified.

3. Strain rate. This final variable is the rate at which the test panel is elongated, usually expressed in percentage of the panel size per unit time. A 10% rate for a 10-cm long panel is an elongation of 1 cm/min or for a 1-cm long panel, 1 mm/min. The strain rate has a similar effect on the flexibility of coating film as does temperature. An increase in the rate is similar to a decrease in temperature. The flexibility of any coating decreases with an increase in the strain rate. Strain rates must be carefully controlled in order to obtain reproducible results, regardless of the method used.

2.1 Determination of Flexibility

The majority of the tests are based on the cylindrical or mandrel tests, in which the coating is applied to a metal substrate and after drying the panel is bent over a mandrel of varying diameter. Elongation of attached organic coatings using a cylindrical mandrel is described in ASTM D 1737, and in Federal Test Method Standard No. 141 (FTMS) Method 6221 and consists of: application of the material to be tested to a cold-rolled carbon steel, conforming to SAE 1010 chemical requirements, 1/32-in. in thickness. The coating is air-dried or baked, depending on the requirements. The coated panel is conditioned at 25 ± 1 C and 50 ± 5% humidity for at least 24 h. The panel is bent over a mandrel of specified diameter through an arc of 180 degrees within one second. The coating is examined using 5X magnifications for any evidence of cracking or delamination from the substrate. A second test is usually run to confirm the results obtained. The test indicates the amount of elongation the coating is capable of, without failure. The relationship between mandrel diameter and elongation can be calculated from the formulation:[2]

$$\%\ \text{elongation} = 100\ \frac{T}{2R + T} \qquad (2\text{-}1)$$

where

T = thickness of metal panel
R = radius of mandrel

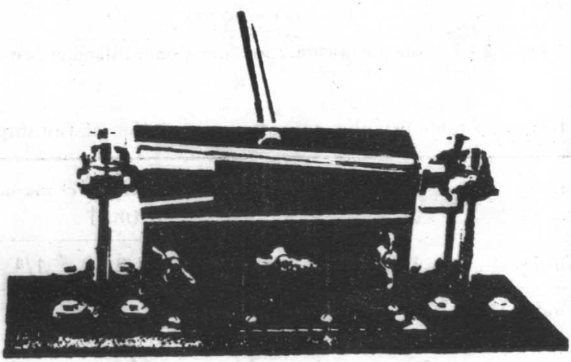

Fig. 2.1 Conical Mandrel Tester (ASTM D 522).

The second most popular test is one described in ASTM D 522, entitled *Elongation of Attached Organic Coatings with Conical Mandrel Apparatus.* The FTMS Method 6222 describes the same method with some slight