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Contact Angle Characteristics and Breaking Strength of Paint Plastic Film

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Synopsis

The advancing contact angle of water on plastic film coatings on metal was measured against both the air and the metal side surfaces after their being peeled off from the metal substrate. The plastic used was a methacrylate copolymer, and it was baked on cadmium, aluminum, nickel, iron, and gold. Contact angle for the air side was about 74° at 25°C. for all metals, but the values on the metal side differed considerably, ranging from 76° for gold to 50° for cadmium. At the same time the static breaking strengths of the same films were investigated by applying a knife-edge vertically to the film with increasing load and measuring the weight at which the electric resistance through the film became zero. Increasing film thickness gave increasing strength, but further thickening made the film weaker with a tendency for crack formation. The film–metal combinations of larger contact angle difference generally also showed the higher breaking strength.

INTRODUCTION

There are many ways of estimating the strength of adhesion of a paint film to a metal surface. However, most of these are mechanical testing methods and very few are physicochemical. The aim of the present paper is to introduce a physicochemical method for measuring the difference in contact angle of water with the air and the metal sides of a paint plastic film. The basic idea is that if a paint film has any special affinity for the metal (or perhaps the metal surface oxide), the nature of the film on the side towards the metal surface should differ considerably from that towards the air surface of the film.

To estimate the difference, contact angle measurements were employed, as Bartell and Ray[1] have reported that the contact angle formed by water against a plastic film is indicative of the degree of hydrophilic or polar nature of the polymer surface.

The other part of the present work is to compare the contact angle results with the results of a common mechanical test. This test was a kind of knife-edge method and consisted of applying a knife-edge vertically to the paint surface with increasing static weight until the electric resistance between the knife and the metal substrate dropped to zero. Fairly good correlation was obtained with polyacrylate paint film between the contact angle difference and the breaking weight.

EXPERIMENTAL

Materials

A clear acrylate copolymer was used which contained 29 wt.-% of butyl acrylate, 18 wt.-% methyl methacrylate, 17 wt.-% styrene, 26 wt.-% *n*-butoxymethylacrylic amide, and 8 wt.-% methacrylic acid. The coated metals were thin sheets of gold, iron, nickel, aluminum, or cadmium of 99.9% purity.

The metal sheets received no surface treatment but were degreased with a suitable cleaning agent and washed with distilled water. These surfaces had a very low contact angle against water. The plastic coating was applied to the surface as an alkaline aqueous solution and, after evaporation of the water, baked by use of infrared radiation at 100°C. for 45 min. This baking temperature was lower than that commonly employed, but in the present experiment the plastics solidified enough to show cracks at the breakdown. The amount of plastics per unit area was adjusted to be suitable for the measurements. The thickness of the baked film was as follows. For the contact angle measurement, the paint film had to be peeled off from the metal sheet by bending the sheet sharply, and this procedure required a film thickness of more than 100 μ. For the knife-edge test, a series of films of various thicknesses ranging from about 15 to 120 μ, was prepared. The thickness was measured with a micrometer.

Contact Angle Measurement

The plastic film peeled from the metal sheet was placed on a glass sheet and a drop of distilled water was formed on the film by use of a micropipet (medical syringe) with a fine tip.

Special care was taken to ensure the metal surface was still wettable with water after the removal of the plastic film. Sometimes the metal surface showed an unusually large contact angle against water. In such cases the film was considered to have been split and the sample was not suitable for measurements.

The angle was measured by means of goniometer telescope. The advancing angles were read with successive increments of water. According to Gaudin and Witt,[2] the advancing angle seems to be an equilibrium one. The measurement was made at 20°C. both on different regions of the same specimen and on different specimens of the same material combination. The scattering of the contact angle values are shown in Table I for the metal

TABLE I
Scattering of Contact Angle Values

	Different regions				
Different specimens	50°	50°	48°	48°	45°
	52°	51°	52°	50°	
	47°	50°	50°	50°	

side of paint film on cadmium, for example. The range of scattering reached 9° with iron, but the difference in contact angle between metals was so wide that the scattering was of no significance in comparing the characteristics.

Measurement of Breaking Strength

Figure 1 shows schematically the knife-edge device used, which is similar in principle to the indentation hardness tester. Instead of the usual pyramid or cone in the latter instrument, a knife edge is used to measure the average strength along the edge. The supporting pole has a hemispherical end, which enables the knife edge to rest on the paint surface. The knife edge was made of tool steel. The angle of the knife edge was 30° and the length of the edge was 1 cm. The tip of the edge was rounded with the radius of 2 μ.

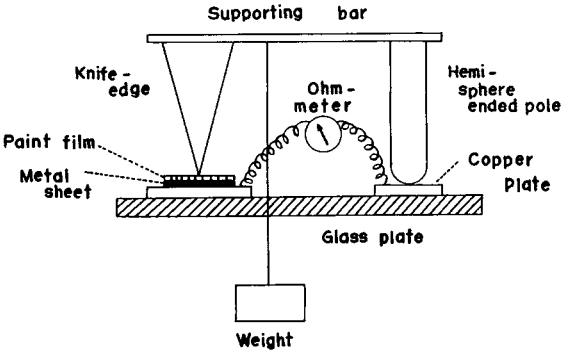


Fig. 1. Schematic diagram of knife-edge device for measuring breaking strength.

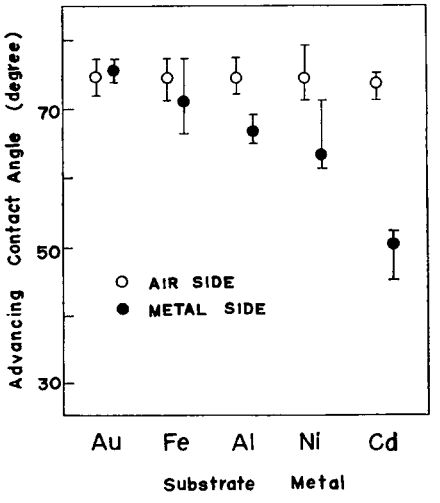
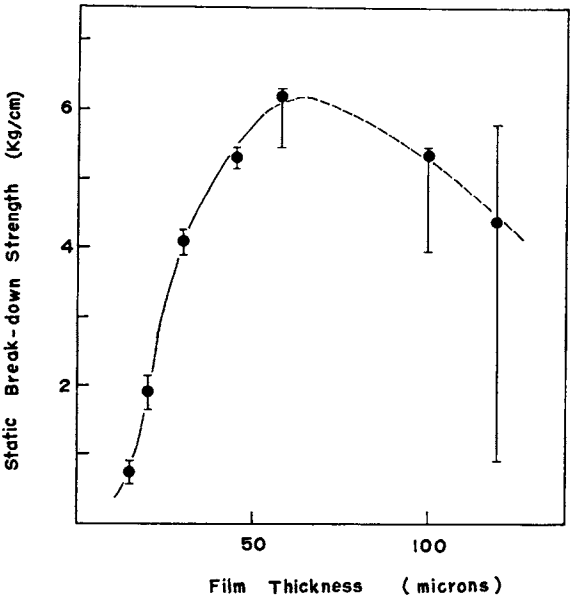


Fig. 2. Contact angle of water against peeled plastic film.



(a)

Figure 3. See caption, p. 301.

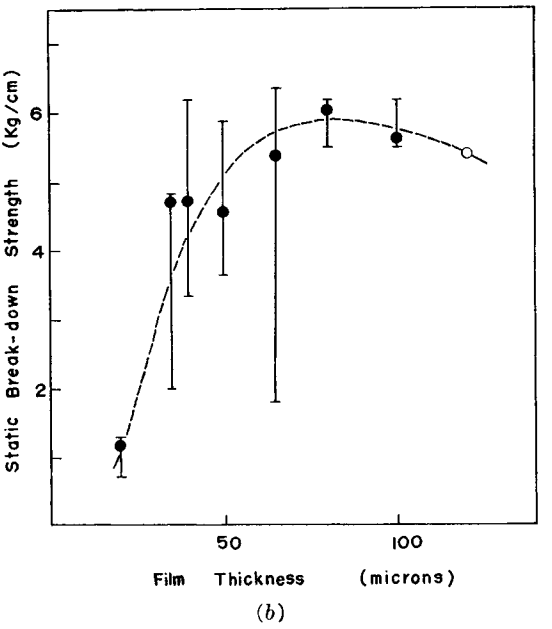
The minimum weight at which the ohmmeter showed almost zero was read at room temperature. Sometimes it took a little time to reach zero resistance after applying a weight. The minimum weight was read at 100 g. increments. Observed values were widely scattered with thicker paint film.

RESULTS

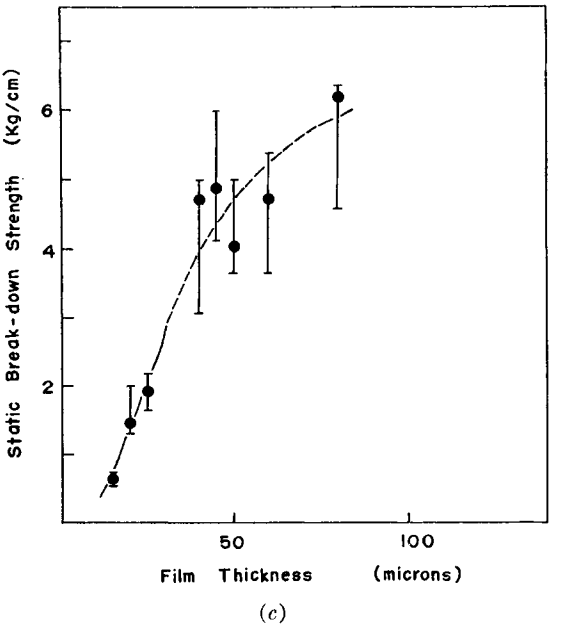
Contact Angle Difference

Figure 2 shows the contact angles of water at 20°C. against both the air and metal sides of the paint films for each metals. Data are indicated by the range and the median. The contact angles against the air side are independent of the kind of metal substrates and range from 79° to 71°; the median is 74.5°. Craig and others[3] reported that the advancing contact angle of water at 25°C. is 78 ± 1° against poly(methyl methacrylate) and 86 ± 1° against polystyrene. Considering that the examined is a copolymer of methacrylate, styrene, and others, the obtained value seems very reasonable.

The contact angles against the metal side are quite different with different metals. In Figure 2 the metals are arranged in the order of increasing contact angle. According to Bowden and Moore,[4] cadmium reacts strongly with fatty acid and slightly with ethyl ester, whereas gold does not react. Lancaster[5] showed that nickel oxide and aluminum do not react with fatty acid but absorb it physically, and nickel adsorbs more



(b)



(c)

Fig. 3. Knife-edge breaking strength of plastic films: (*a*) on cadmium; (*b*) on aluminum, (*c*) on iron.

strongly than aluminum. These facts can explain very satisfactorily the present results. The iron oxide is reported to react slightly with fatty acid; it is not clear why iron is between gold and aluminum in values.

Static Breaking Strength

The minimum weight data had to be calibrated because the weight that worked at the edge was the weight of the knife-edge itself, 190 g. plus, as is easily seen, the measured weight times the arm ratio, 1.5, of the lever.

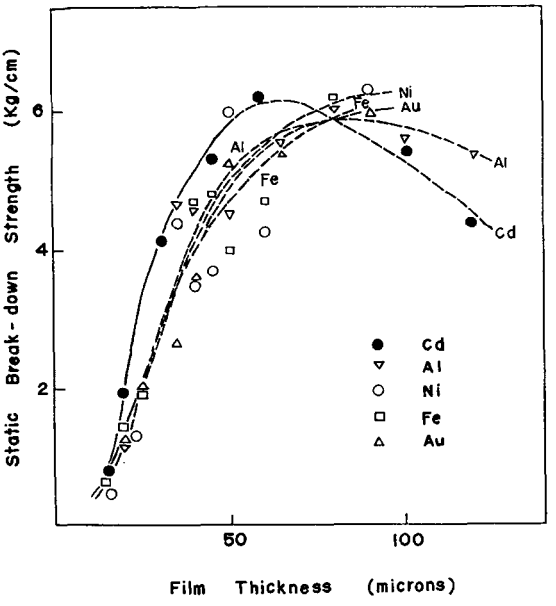
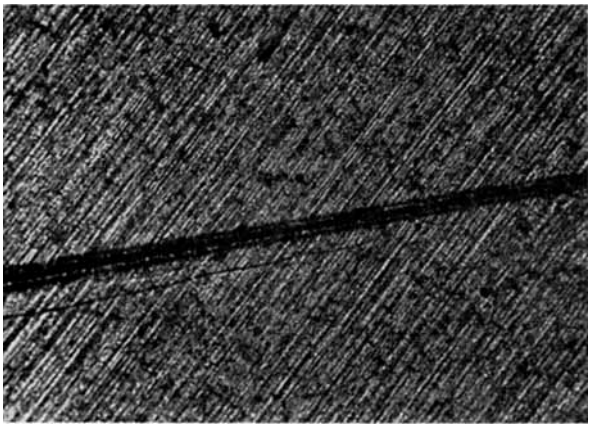


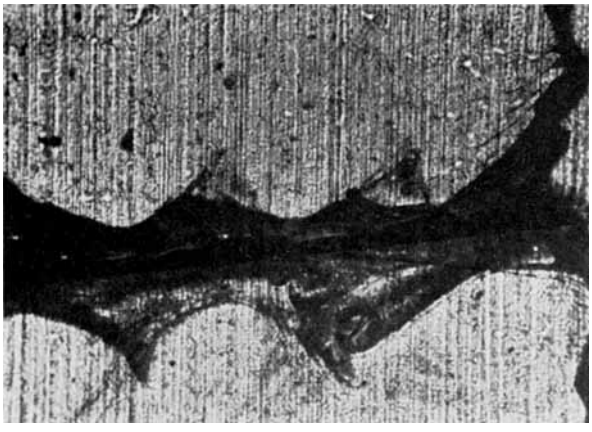
Fig. 4. General trend of knife-edge breaking strength.

In Figures 3*a*, 3*b*, and 3*c* the ranges and the medians are plotted against the film thickness with cadmium, aluminum, and iron, respectively. The solid line shows the general relation between the film thickness and the static breaking strength; the broken line indicates the region in which the data showed considerable scatter; the values were less reliable. Figure 4 gives the medians and the characteristic lines of all film–metal combinations.

There are some interesting findings. The first is that the breaking strength increases with film thickness to a maximum at about 60–80 μ. Secondly, in the above range of thickness the film on cadmium is strongest, and the data show little scatter compared with the others. Thirdly, the film strength seems to decrease or remain constant in the thicker region, where the film on cadmium is weakest. Asbeck[6] studied removal of coatings with a knife, and found that the removal force first increases proportionally to the film thickness for thinner films and then abruptly decreases and fluctuates with cracking of the film. In the present work nearly the same characteristics were observed. Figure 5 shows the cut obtained with thin films and the cracking break with thick films on cadmium.



(*a*)



(*b*)

Fig. 5. Trace of knife edge: (*a*) simple cut; (*b*) cut with cracking.

DISCUSSION

As already mentioned, the contact angle difference is largest with the film on cadmium, which probably reacts with the functional groups of the polymethacrylate, and smallest with gold. Therefore, the contact angle difference can be regarded as a measure of adhesive strength of the polymer film to the metal substrate. In addition, a large difference in contact angle means that the nature or molecular structure of the film on the air side differs markedly from that on the metal side,[7] so that the mechanical stress in the film is also largest.

These facts make it obvious why the thin film on cadmium are strongest and why thick films breaks with cracking. It is found that the order of contact angle difference in Figure 2 is in fairly good agreement with that of thin film strength.

The proposed loading knife-edge method to measure the strength of paint film seems to work well. The characteristics of this method is its static nature and simplicity. There may be a potential applicability to studies of rheological properties of paint film, if measurements are made with several edges of different angles.

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Résumé

L'angle de contact en avancant sur l'eau a été mesuré au contact de l'air et à la surface métallique d'un film de plastique peint après qu'il ait été pelé de la surface de substrats métalliques. Les plastiques était un copolymère de méthacrylate et cuit sur cadmium, aluminium, nickel, fer et or. L'angle de contact par rapport è l'air était d'environ 74° à 25°C pour tous les métaux mais par rapport au métal différé considérablement, variant de 76° pour l'or à 50° pour le cadmium. De même la force statique de rupture du film peint a été étudiée en appliquant verticalement une pointe de canif sur le film avec un point croissant et mesurant le poids auquel la résistance électrique au travers du film devient nulle. L'accroissement de l'épaisseur du film donnait une force accrue mais un épaississement ultérieur rendait le film plus mou avec formation de craquelures. Une tendance génera e a été observée de la combinaison film–métal avec une différence d'angle de contact plus grande permet l'obtention d'une force plus élevée à la rupture.

Zusammenfassung

Vorrückende Kontaktwinkel von Wasser wurden gegen die Luftseiten-und Metallseitenoberfläche von Plastomeraufstrichfilmen nach Abziehen vom Metallsubstrat gemessen. Als Plastomers wurde ein Methacrylatcopolymeres, das auf Cadmium, Aluminium, Nickel, Eisen und Gold aufgebracht wurde, verwendet. Der Kontaktwinkel gegen die Luftseite betrug für alle Metalle etwa 74° bei 25°C, derjenige gegen die Metallseite zeigte dagegen beträchtliche Unterschiede und lag im Bereich von 76° für Gold bis 50° für Cadmium. Gleichzeitig wurde die statische Beanspruchungsfestigkeit durch Einwirkung einer Messerkante vertikal zum Film unter steigender Belastung und Messung des Gewichts, bei welchem der elektrische Widerstand durch den Film Null wurde, untersucht.

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