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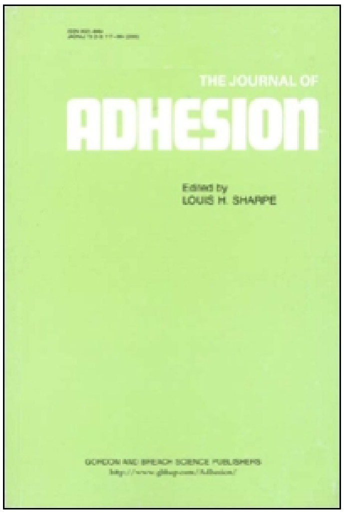

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NOTE

Interpretation of Adhesive Forces In Electroplated Polypropylene

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A short description of the electroplating process of plastics and its mechanism is presented. Studies to determine what type of bond is responsible for the adhesion between polypropylene and electrolytic metal plate are reported. Micrographic studies seem to discard an important contribution of the "mechanical" bond. Multiple infrared reflectance spectra and contact angles did not detect polar groups caused by the electroplating process. These findings are considered an indication that dispersion forces (induced dipole-induced dipole interactions) are the main contributor to the adhesion of electrolytic metallic plate to polypropylene substrate.

INTRODUCTION

BEFORE BEGINNING the discussion of the attempt to interpret the adhesion forces effective between the metal plated on polypropylene by electrolytic methods, a short and general description of the electroplating process for plastics and its mechanism seems to be in order.

On Figure 1 the first step is designated as pretreatment. Whether annealing or cleaning is necessary depends on two things—the type of plastics dealt with, and within a given type of plastics, the problems introduced by faulty molding conditions and mold design. If the above-mentioned problems exist, annealing or other pretreatment methods may abolish or decrease them to a tolerable level.

The second step, which is termed "conditioning", can be described as "chemical etching" in a bath consisting of a solution of CrO_3 in strong inorganic acids. The chemical etch increases the adsorptivity of the plastic surface, which is essential for the next step. The chemical reaction taking place in the conditioning bath could be classified as an oxidation of the plastic substrate and reduction of Cr^{+6} to Cr^{+3}.

The third step, "sensitization" and "activation", involves the adsorption of a reducing agent (sensitizer) and the adsorption of a noble metal ion (activator). The subsequent reaction is the reduction of the noble metal ion (mostly palladium) to the metal, which then remains deposited on or in the plastic surface.

Step number four is the electroless plating step. The plastic object with noble metal particles adsorbed on its surface is dipped into either a *copper salt solution* or a *nickel salt solution*. Immersion times and temperatures depend on the compositions of the baths. In accordance with its position in the electromotive series, the metal will plate out on palladium.

The fifth and last step is electrolytic plating. There are two basic systems, as shown in Figure 1. The first consists of a plate of copper followed by a plate of (bright) nickel and then by a plate of chromium. The second has a plate of semibright nickel followed by bright nickel plate and then by chromium.

Thanks to the relative straightforwardness of the electroplating method, its mechanism became established in an early stage of plastics plating research and is summarized in Table 1.

Figure 1. Electroplating process

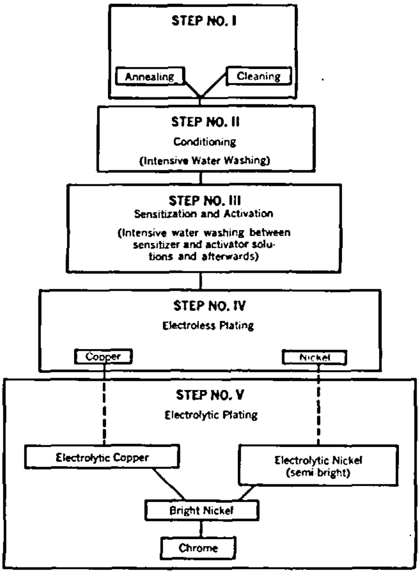


Table 1. Steps in the Electroplating Process

Steps	*Dependence on the Type of Substrate Used*	*Mechanism*
I. Pretreatment	The choice and use of the pretreatment systems depends on type of plastic and molding conditions.	Pretreatment, conditioning and etching produces an absorptive surface.
II. Conditioning	The use and choice of the conditioner depends on type of plastic used and molding conditions.	
III. Sensitization and Activation	Independent of the plastic used.	Diffusion of metallic ions (one of them a noble metal ion) and of reducing agents takes place into the surface. The noble metal ion is reduced to metal. Cu and Ni plate out on the noble metal.
IV. Electroless Plating	Independent of the plastic used.	
V. Electrolytic Plating	Independent of the plastic used.	Usual mechanism as known in metal plating.

THEORY

The interpretation of bonds involved in the adhesion of the metal to the plastic proved to be far more complicated.

Two types of bonds are possible, the mechanical and the (physico) chemical. We can see from micrographs that a schematic sideview of an etched surface is either

or

If a significant mechanical bond were present, the etched surface should show the following side view:

On the other hand, we know that through aging the adhesion of the metal plate to the plastic almost always improves, a fact which indicates interdiffussion of plastic molecules and metallic atoms. This might create steric phenomena which could come under the heading of mechanical bond. Micrograph No. 1 shows at a 750x magnification the cross section of an electroless nickel deposit on etched polypropylene which suggest the point that the mechanical bond, if present at all, does not contribute much to the overall adhesion.[1]

The chemical bond formed between plastic and metallic atoms can be interpreted as the consequence of an electrostatic interaction between the positive nuclei of the atoms in plastic molecules and of the metal atoms with their respective electron populations. Such an interaction might be described as:

> Dispersion forces (induced dipole-induced dipole interaction).
>
> Permanent dipole interaction (including multipole and permanent dipole-induced dipole interaction).
>
> Hydrogen Bond formation (as defined by Latimer and Rodebush).[2]
>
> Direct Valence Bond (including the covalent and ionic bond).

No direct valence bond is possible between a metal in its metallic state (or zero valence state) and the plastic. Occurrence of hydrogen bonds between a metal in its metallic state and a carbon atom or any other element which might be a component of the plastic, such as nitrogen, sulfur, or halogen in the sense as coined by Latimer and Rodebush is not feasible. On the other hand, within the framework of induced dipole-induced dipole interaction, the hydrogen atoms certainly contribute to the overall adhesion. Only the possibilities of dispersion forces and/or regular dipole interactions remain to be considered. The dipoles if present are produced during the etching process and we might expect them to be $-OH$, $>CO$, and $-COO^-$ groups. It seemed that analytical evidence of presence or absence of these groups could decide what type of bond we have in plated plastics.

EXPERIMENTAL

A. Evidence Obtained By Infrared Multiple Reflectance Spectra.

The regions investigated by I.M.R.S. were between the surface and that polymer lying about 0.5 μ-2μ below the surface. We examined several polypropylene and ABS samples etched in commercial conditioners at different etch temperatures ranging from 100°-190°F. We did not find groups which could be attributed to the etching process either in ABS or in polypropylene. However, we found the following: We included in our polypropylene resin about 0.2% of a compound with well recognizable polar groups. Before etching, these groups were easy to detect with I.M.R.S. After we etched the resin blend, we could no longer see polar groups. With ABS we also found something worth mentioning; namely, that after etching we were able to see a definite reduction in the acrylonitrile peak. We did not consider our investigations conclusive enough for, as already mentioned, we were not able to investigate the immediate surface.

B. Evidence Obtained By Contact Angle Studies.

The contact angle between water and polypropylene will decrease if $>CO$, $-COO^-$ and $-OH$ groups are introduced in the surface of polypropylene either through oxidation or grafting. Further, the degree of smoothness or roughness will change the contact angle. The roughness contribution to the change of the contact angle is given by the Wenzel formula[3] which is:

$$r = \frac{\cos\theta}{\cos\theta^1}$$

where

$$r = \frac{\text{apparent area}}{\text{true area}} = \frac{\text{unetched area}}{\text{etched area}}$$

with θ = contact angle before the etch and θ^1 = contact angle after the etch. The equation demands that if θ is less than 90°, $\theta < \theta^1$ and if $\theta < 90°$, $\theta^1 < \theta$.

The preparation of sample plaques (2 x 2.5 x .125 inches) for measurement was done by washing them for 10 minutes in warm tap water (120°-140°F) and then rinsing with distilled water. After the washings, the samples were dried for 30 mins. in the oven at 195°F and cooled for at least one hour in a desiccator. The contact angle (advancing) was measured with the NRL contact angle goniometer model A100 manufactured by Ramé-Hart, Incorporated. The readings were taken within 30 seconds of drop formation. The drop volumes were 0.1 ml.

We measured the contact angle before and after etching on three different polymer types: Nonplatable grade polypropylene Avisun (1016); Moderately platable grade polypropylene Avisun (TD-253A); Easy platable grade polypropylene Avisun (TD-270A). The physical and chemical properties of these three polypropylene grades fall within the range of the commercial specifications generally accepted for polypropylene resins. The differences among the three grades are their etching characteristics. The etching was done with two different conditioners: A conditioner designed for polypropylene (GDO-37, Avisun-Enthone Conditioner) and a conditioner designed for ABS (473, Enthone Conditioner) at 110°F, 140°F, 150°F, 170°F, and 190°F. Five plaques of resin were used for each temperature.

Table 2.

Conditioner GDO-37

		Temperature (°F)								
Resin	*Before Etch*	*110*	*140*	*150*	*170*	*180*	*190*	*210*	*230*	*250*
TD270A	*81.9	75.9	57.8	51.1	94.3		130.3			
	**±2.9	±2.0	±3.3	±4.3	±5.4		±4.7			
1016	*84.6	83.2	82.5	82.3	79.4		74.8			
	**±2.4	±2.3	±3.2	±2.1	±2.7		±5.3			
TD253-A	*82.1	77.9	73.0	66.5	90.0		120.3			
	**±3.2	±2.3	±2.9	±4.6	±3.5		±4.9			

Conditioner 473

		Temperature (°F)								
Resin	*Before Etch*	*110*	*140*	*150*	*170*	*180*	*190*	*210*	*230*	*250*
TD270A	*81.9	75.1	72.7	82.4	94.4	108.8	119.9			
	**±2.9	±2.9	±2.7	±3.6	±3.6	±5.2	±3.6			
1016	*84.6	82.7	79.8	76.8	73.2		86.0			
	**±2.4	±2.3	±1.9	±1.6	±3.8		±2.0			
TD253-A	*82.1	75.5	75.6	72.8	65.2	62.6	54.8	35.6	64.7	110.7
	**±3.2	±3.6	±1.9	±3.0	±2.9	±3.1	±3.1	±2.5	±22.2	±15.0

*Water Contact Angle (Degrees)

**Standard Deviation

The study was made with samples molded about three to four months before the study began, and was conducted as follows:

Every sample was molded so that one side was dull and one side was glossy. On every sample, six contact angles were measured, three on the dull and three on the glossy side. From each temperature, conditioner, resin and side combination after etching, we had fifteen angles. From each resin and side combination before etching, we had 150 angles. Then averages and standard deviations were calulated on an Olivetti Programma 101. We saw that the difference between the sides was insignificant so that in Table 2 the standard deviation was calculated for each resin before etching from 300 angles and for each temperature, conditioner and resin combination from thirty angles. This table should give an indication as to how trustworthy the contact angle measurement is for samples of the same batch and the same molding age.[4] We can see that in the temperature range of 110°F to 190°F the standard deviation is reasonably small. In case of higher temperatures such as 230° and 250°F, the standard deviation is too high for the data to be meaningful.

After the contact angle study was performed, two samples from each combination of temperature, conditioner and resin were plated and the adhesion tested, and two samples were set aside for micrography.

The Jacquet Test[5] was performed to determine the adhesion. The copper metal plate was about 1.5-2.0 mil thick. A standard tensometer was used. A superficial examination revealed that polymer was present on the peeled metal plate even at low (1-2 pounds) peel strength. Further investigation is planned.

Figures 2 and 3 show us the contact angles and the corresponding peel test results.

We expected the contact angle to decrease after etching because of:

Increase of hydrophilic groups (OH, CO)
Increase of the surface area.

The reason for expecting the increase of the surface area to contribute to the decrease of the contact angle was that all three grades showed a contact angle of below 85° before etching. Therefore, according to Wenzel's equation, we had to expect a decrease in the contact angle due to surface roughness. The results were not quite as we expected; Avisun grade 1016 which is nonplatable behaved normally, that is, it was not etched as we can see on the micrographs and it did not display any extreme changes in contact angles. TD-253A and TD-270A, the platable grades, in both conditioners showed a completely different behavior. At first, the contact angle decreased but after reaching a minimum value, the contact angle sharply increased as can be seen on Figures 2 and 3.

Figure 2.

Contact angle dependence on etching temperature.

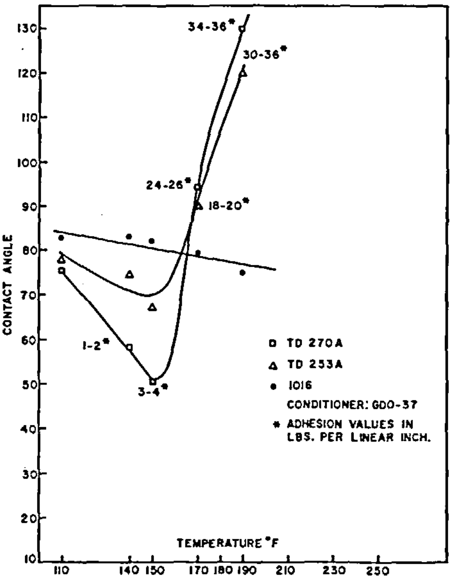
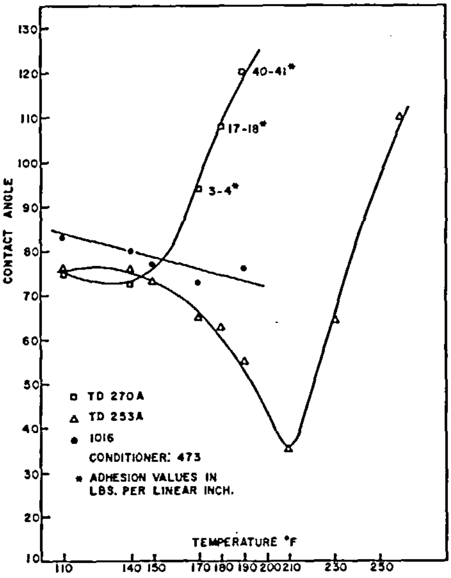


Figure 3.

Contact angle dependence on etching temperature.



It is interesting to note that in the case of ABS, the contact angle always decreases which is in complete accordance with the Wenzel formula. The samples of ABS we investigated had a contact angle of 65-80° before etching and after the etching, optimum adhesion values were obtained at a contact angle of 20-35°.

C. Evidence Obtained By Micrograph Study.

The following list compares some of the contact angles with corresponding micrographs and adhesion values.

Micrograph No.	*Adhesion Value in lbs./inch.*	*Resin*	*Conditioner*	*Contact Angle (deg.)*	*Temp. °F.*
2	0	1016	473	84	110
3	0	1016	473	75	190
4	0	TD-270A	473	75	110
5	17-18	TD-270A	473	110	180
6	40-41	TD-270A	473	120	190
7	30-36	TD-253A	GDO-37	120	190

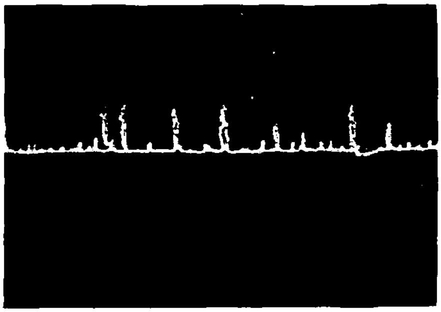
From these and other micrographs, it became obvious that within the same resin and conditioner system the heaviest etching coincided with the highest adhesion value and the highest contact angle.

DISCUSSION AND CONCLUSIONS

At the beginning of the paper, we pointed out that the chromic acid treatment (Step No. 1, Figure 1) is essentially an oxidation of plastics. We have not found any spectral evidence of remaining carbonyl, carboxyl or hydroxyl groups. A possible explanation might be that in the case of a mild oxidation which would be in the temperature range of 100-130°F those mentioned groups were situated on or in the immediate surface of the investigated samples and we were not able to detect them. In case of a severe oxidation, which would take place at temperatures higher than 152°F, we have a complete oxidation of the plastics to CO_2 and H_2O, and the few remaining groups escape detection. It has been reported in the literature[6] that treatment of crystalline polypropylene by high concentration of chromic acid at 158°C for prolonged periods of time (100 hours) will remove layers of polypropylene without causing a change in its infrared spectrum. We should also keep in mind that polypropylene more than any other commercial plastics has the largest number of tertiary carbon atoms per polymer molecule. Tertiary carbon atoms in severe oxidation conditions will yield easily to a complete oxidation to CO_2 and H_2O.

Our contact angle and micrograph study support the above-mentioned explanations. As we can see at mild conditions (110°F) neither the nonplatable nor easy platable resin (Micrographs 3 and 4) show any etching, but the contact angles are definitely decreasing (Figures 2 and 3).

What does the increase of contact angle mean in case of etched polypropylene? Because of Wenzel's formula, the most plausible explanation is that the conditioner "cleans" the polypropylene surface of all modifications and additives and so elevates the original contact angle θ above 90° and because

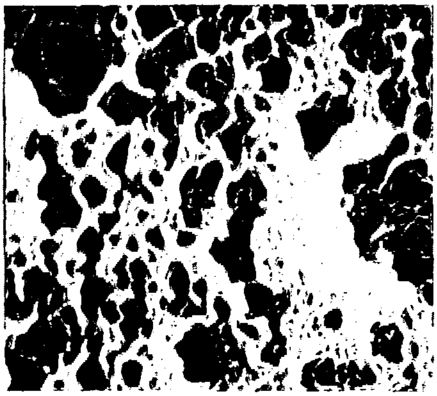


Micrograph 1. Magnification 750X. Cross section of an electroless nickel deposit on etched polypropylene. 1

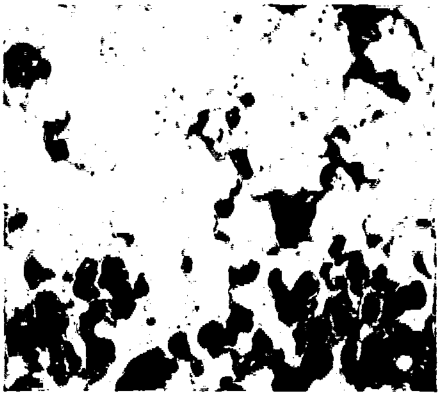
Micrograph 2. Magnification 3000X. View of an unplatable polypropylene type etched at 110°F in an ABS conditioner.

Micrograph 3. Magnification 3000X. View of an unplatable polypropylene type etched at 190°F in an ABS conditioner.

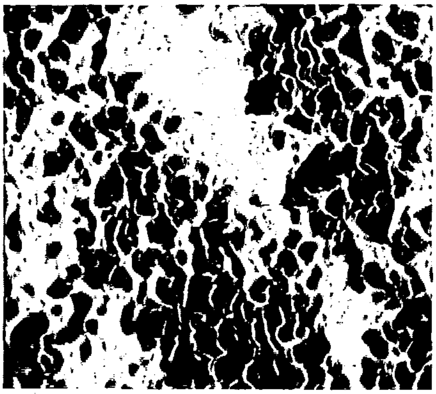
Micrograph 4. Magnification 3000X. View of an easy platable polypropylene type etched at 110°F in an ABS conditioner.



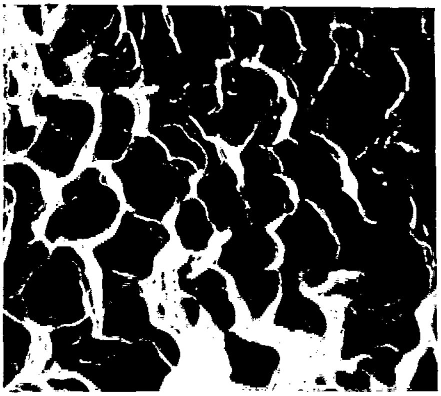
Micrograph 5. Magnification 3000X. View of an easy platable polypropylene etched at 170°F in an ABS conditioner.



Micrograph 6. Magnification 3000X. View of an easy platable polypropylene etched at 180°F in an ABS conditioner.



Micrograph 7. Magnification 3000X. View of a moderately platable polypropylene etched at 190°F in a special polypropylene conditioner.



Micrograph 8. Magnification 10,000X. View of a moderately platable polypropylene etched at 190°F in a special polypropylene conditioner.

of the roughness of the surface, the angle after etching θ^1 increases significantly. We measured the contact angle on "pure" polypropylene and found it to be around 92°. Possibly if we would have taken more precautions such as melting in an N_2 atmosphere, we might have obtained still a higher angle.

It is worthwhile to note that polypropylene gives higher adhesion values than ABS although the wettability of the latter after etching is far superior. ABS obtains its optimal adhesion value of about 10-12 pounds per inch at a contact angle value after etch of about 30°. Polypropylene shows good adhesion values of 20-30 pounds per inch at a contact angle of 130° after etch. The significance of wettability for adhesives and adhints is well documented in the literature[7]. As far as we know, similar documentation of the role of wettability for electroplating on plastics has not yet been published. Therefore, we prefer to postpone any conclusion about the importance of wettability for electroplating processes until more data are available. Especially important will be contact angle values of liquids other than water on etched polypropylene and ABS. Such a study has been initiated in this laboratory and will be reported on in due time. Looking at Table I we see that the phenomenon of diffusion is essential for the electroplating process. The first two steps, pretreatment and conditioning, increase the adsorptivity of the surface. The next two steps, treatment of the etched substrate with noble metal ions and reducing agents and production of a conductive coating, are based on the successful diffusion of metal ions into the substrate. The increase of adsorptivity of the substrate is produced by converting the smooth surface into a porous one. The frequency of the pores and the depth of the pores are two variables which, if measured, would provide us with a fair possibility of predicting possible bond strength between plastics and metal. We may consider the frequency of the pores or roughness and use the contact angle as a roughness parameter.

Because those who electroplate plastics are very much in need of nondestructive easily measurable parameters which indicate platability, we intend to investigate further how far contact angles might be of service for this purpose.

Summarizing, two conclusions may be drawn:

1. Polar groups in etched polypropylene are not detectable either on the surface through contact angles studies, or in regions about 0.5-2 microns below the surface by infrared multiple reflection spectroscopy. This might be considered as strong evidence that the main contribution to the adhesion of the metal plate to the plastics is made by dispersion forces.

2. The concurrence of the strongest etch, highest contact angle and the highest adhesion suggest the possibility that the contact angle might be the easiest measurable variable to predict bond strength immediately after the etching of the object in question.

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Mrs. E. G. Shafrin and Mr. W. D. Bascom, both from the Naval Research Laboratory, have been very helpful in practical suggestions about contact angle measurements and where to obtain the necessary tools to perform them. Mr. Warren R. Doty from Udylite Research was so kind as to supply Micrograph No. 1. Dr. J. L. Jezl and Mr. H. M. Khelghatian, both from Avisun Corporation, have allowed the necessary time and have given many useful suggestions. Mr. A. J. Lutz did most of the measurements and the standard deviations calculations.

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