Iodine Treatment of Nylon: Effect on Metal Plating of the Polymer*

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Synopsis

The iodine treatment of nylon surfaces consist essentially of dipping the nylon in an iodine–potassium iodide solution and quickly rinsing the absorbed iodine out of the nylon surfaces using glycol–water–thiosulfate as a wash solution. The treatment was found to profoundly affect the adhesion between the nylon and an electrolessly deposited metal on its surface. The adhesion changes from no adhesion for an untreated nylon surface to a maximum of 28 lb/in. for a treated sample. The adhesion is dependent mainly on the nature of the nylon surface (crystallinity, molecular weight, etc.), the duration of the iodine treatment, and the nature and conditions of the wash solution. Electron microscope pictures of the nylon surface after the iodine treatment show a shallow etching pattern, and therefore mechanical keying between the metal and the polymer is not a probable factor of importance. Under certain experimental conditions, the iodine treatment changes the crystallinity from the α-form predominant in the nylon before treating the sample to the γ-form. It also decreases the overall crystallinity of the surface, softens the polymer, and improves its water wettability. All the above changes enhance a more intimate interaction between the deposited metal and the polymer.

INTRODUCTION

Metal plating of nonconductive surfaces consists of chemically depositing a metal layer on the surface of the nonconductive material followed by electrolytic deposition of the desired metal or metals for decorative or functional end uses. The essential step in the technique of plating plastics lies in modifying their surfaces to accept and adhere to the chemically deposited (electroless) metal. Goldie[1] summarizes the variety of treatments used for different polymers in order to accomplish such a modification.

The nature of the metal-to-polymer adhesion has been the subject of speculation and study for the past several years. Some content that it is a mechanical adhesion governed mainly by the degree and the nature of porosity created on the modified polymer surface. Kato,[2] Matsunaga and co-workers,[3] and Heynmann[4] in their studies of ABS (acrylonitrile–butadiene–styrene terpolymer) treated in a chromic acid solution have indicated that the adhesion of the metal to the polymer seems to be a function of the type (dovetail or stud) and degree of porosity of the polymer surfaces. In spite of their experimental findings, Matsunaga and co-workers[3] contend

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* Patent applied for.

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that chemical bonding between the metal and the polymer surfaces must be considered. Other workers have also provided evidence that chemical interaction between the deposited metal and the polar groups generated on the polymer surface after treatment play a major role in the bonding.[1,5,6]

This paper describes a novel system for the modification of nylon surfaces to accept metal plating. As will be shown, the treatment imparts only a shallow etching pattern to the surface of the nylon and yet it leads to a dramatic change in the bonding strength between the polymer and the deposited metal. Previous attempts at plating of the nylon involved using a glass-filled grade of the polymer and roughening its surface in a water and pumice slurry.[7] There is no evidence that such a treatment leads to good adhesion between the nylon and the metal.

EXPERIMENTAL

Materials

Most of the work described in this paper was performed on plaques of nylon 6, polycaprolactam, bulk polymerized, using sodium hydride as a catalyst and polyisocyanate as a cocatalyst. This method yields highly α-crystalline nylon 6. Plating evaluations were also carried out on another type of nylon 6 similarly polymerized but with a different proprietary cocatalyst system as well as on nylon 66 plaques obtained from the du Pont Company. All other chemicals used were analytical-grade reagents.

Plating Procedure and Testing

The iodine treatment of nylon surfaces was performed by placing the nylon in an iodine–potassium iodide solution 0.25 to $0.5M$ with respect to iodine. The bath was used at temperatures varying between 20° and 45°C. The duration of the treatment also varied between 0.5 and 5 min. The iodine was then quickly washed out of the nylon by placing the sample in an ethylene glycol–water–sodium thiosulfate solution containing 5–25% (v/v) water and 3 g/l. $Na_2S_2O_3 \cdot 5H_2O$. The temperature of the wash bath was varied between room temperature and 80°C to obtain optimum conditions. Another washing bath which was used consisted of 50/50 (v/v) acetone–water solution containing 3 g/l. $Na_2S_2O_3 \cdot 5H_2O$. The temperature of the bath was room temperature. The samples were kept in the washing baths until the iodine was thoroughly washed out. For most samples the washing time was 4 min. However, a washing time of 20 min was sometimes required.

After the above iodine treatment, samples of nylon were thoroughly washed with water and placed in a palladium chloride solution containing 0.26 g/l. palladium chloride and 4.50 ml/l. hydrochloric acid. In this bath, reduction of palladium ion to palladium metal occurs at the surface of the nylon. The palladium metal will act as a catalyst for the deposition of nickel from an electroless nickel bath. The duration of the treatment in the palladium chloride was 3 min, after which the sample was thoroughly

washed with water and placed in the electroless nickel bath for a period of 8 min.

In order to obtain adhesion values between the metal and the plastic, 2 mils of copper electroplated from an acid solution was uniformly plated on the surface of the electroless nickel plated plaques. The samples were aged for a period of not less than 48 hr, and grooves, 1 in. apart, were cut through the metal plating and to the polymer surface. The Jacquet test[8] was then applied using an Instron Universal Tester to measure the peel strength at a cross-head speed of 1 in./min.

Surface Studies

To characterize the nature of the nylon surface before and after the iodine treatment, a scanning electron microscope (Cambridge Stereoscan) and a transmission electron microscope (Siemans Elmiskop I) were used. The routine resolution on the latter is 10 Å. Also FMIR (Frustrated Multiple Internal Reflectance) spectra of the surface were taken using an infrared spectrophotometer (Perkin Elmer 621). A Tukon instrument was used to measure the Knoop hardness of the surface before and after the iodine treatment.

RESULTS AND DISCUSSION

In plated plastics, the bonding between the metals and the untreated polymeric surface is in most cases very poor. In order to promote such a bonding, most systems rely on an oxidative treatment that will generate polar groups on the surfaces of the polymer and in many cases produce a pronounced etching pattern. The iodine treatment for nylon differs from existing treatments in that it is nonoxidative and does not impart any appreciable etching on the surface of the polymer. However, it does drastically affect the adhesion between the nylon and the deposited metal, as shown in Table I. Without the treatment, essentially no adhesion exists between the nylon and the metal; and, as is shown, an adhesion value of greater than 25 lb/in. could be obtained under optimum conditions of the treatment.

The optimum conditions for the iodine treatment depend on the nature of the nylon, molecular weight and crystallinity of the surface being the governing factors. The quenched samples of nylon, or the compression-molded nylon, have a lower α-crystallinity than regularly cast nylon and are more easily penetrated by the iodine solution, thus making the optimum iodine treatment conditions less severe, as indicated in Table I. X-Ray diffraction patterns of cast nylon, injection-molded nylon, and quenched nylon 6 are shown in Figure 1. Molecular weight differences coupled with differences in crystallinity exist between the nylon 6 cocatalyzed by polyisocyanate and those prepared using the proprietary cocatalyst. As such, the optimum iodine treatment and the resultant metal-to-polymer adhesion are different for the two cocatalyst systems (see Table I).

TABLE I
Adhesion Values Between Metal and Nylon Surfaces

| Sample	Thickness of sample, in.	I$_2$ Treatment conditions			
		I$_2$ (temp., °C), min	Nature of wash solution	Minutes in wash solution (temp., °C)	Average peel strength, lb./in. strip
1. Nylon 6, polyisocyanate cocatalyst	$^1/_8$ (untreated)	0	Acetone/water (50/50)	5 (R.T.)	0
2. Nylon 6, polyisocyanate cocatalyst	$^1/_8$ (optimum)	0.5 (R.T.)	Acetone/water (50/50)	5 (R.T.)	7.5
3. Nylon 6, polyisocyanate cocatalyst	$^1/_8$	1 (R.T.)	Acetone/water (50/50)	5 (R.T.)	5.6
4. Nylon 6, polyisocyanate cocatalyst	$^1/_8$	2 (R.T.)	Acetone/water (50/50)	5 (R.T.)	4.4
5. Nylon 6, polyisocyanate cocatalyst	$^1/_8$ (optimum)	0.5 (R.T.)	Ethylene glycol/water (80/20)	4 (60°C)	28.0
6. Nylon 6, polyisocyanate cocatalyst	$^1/_8$	1 (R.T.)	Ethylene glycol/water (80/20)	7 (60°C)	25.0
7. Nylon 6, polyisocyanate cocatalyst	$^1/_8$	5 (R.T.)	Ethylene glycol/water (80/20)	20 (60°C)	15.0
8. Nylon 6, polyisocyanate cocatalyst	$^1/_4$ (optimum)	2 (45°C)	Ethylene glycol/water (80/20)	7 (81°C)	12.3
9. Nylon 6, proprietary cocatalyst	$^1/_8$ (optimum)	2 (44°C)	Ethylene glycol/water (80/20)	8 (81°C)	8.0
10. Nylon 6, proprietary cocatalyst	$^1/_4$ (optimum)	2 (45°C)	Ethylene glycol/water (80/20)	10 (81°C)	2.0
11. Nylon 6, proprietary cocatalyst	$^1/_2$ (optimum)	2 (45°C)	Ethylene glycol/water (80/20)	8 (80°C)	0.9
12. Nylon 6, proprietary cocatalyst (quenched)	$^1/_2$ (optimum)	0.5 (R.T.)	Ethylene glycol/water (80/20)	8 (80°C)	3.3
13. Nylon 66, compression molded	$^1/_8$	0.5 (R.T.)	Acetone/water (50/50)	5 (R.T.)	4.0
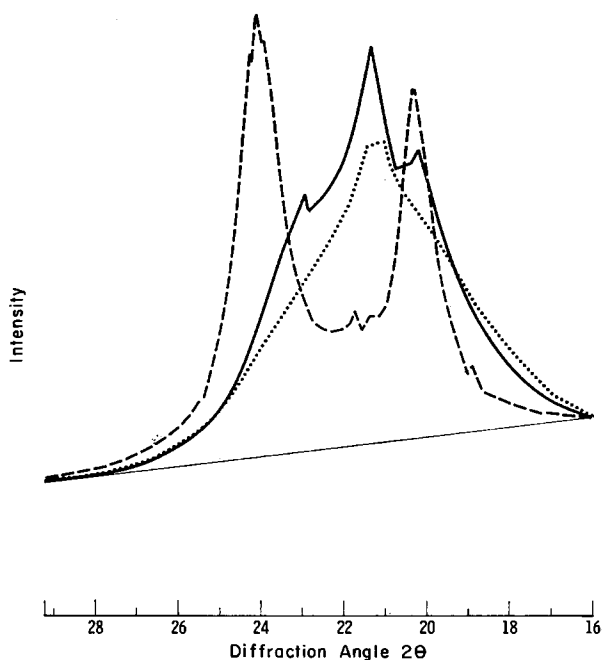
Fig. 1. X-Ray diffraction patterns of nylon 6: (- -) cast; (———) injection molded; (...) cast and quenched.

The decrease in adhesion values with increase in thicknesses of the plaques is probably due to differences in the crystallinities caused by differences in the thermal history of thick and thin samples.

In most plated plastics, the adhesion between the metal and the polymer has been attributed to the formation of a uniformly porous surface on the polymer, thus allowing mechanical keying or interlocking of the deposited metal to the etched plastics surface.[2,3,4,15] A polymeric surface where such mechanism of adhesion is possible is shown in Figure 2. The figure shows a surface of polypropylene etched in chromic acid. The polypropylene is a special plating-grade polymer developed at General Motors Research Laboratories. The iodine treatment does not impart such a drastic etching pattern to the nylon (see Fig. 3). Part (a) of the figure shows an untreated nylon 6 surface, while part (b) shows an iodine-treated surface. Both micrographs were taken under similar conditions as in Figure 1.

In order to obtain a better resolution of the microstructure of nylon 6, a transmission microscope was used. Figure 4 shows micrographs of the nylon surfaces before and after the iodine treatment using the transmission electron microscope. It is evident from Figures 3 and 4 that the surface of the nylon after the treatment is more uniform than before and that the etching pattern, although thorough and uniform, is shallow. Therefore the mechanical keying of the metal to the polymer can be excluded as a mechanism of adhesion in this polymer. Similarly, the etching pattern of

nylon 66 shown in Figure 5, although different from that of nylon 6, is still very shallow and cannot provide for interlocks between the polymer and the metal. The etching pattern on the nylon surfaces could, however, explain the diminished light reflectance and the enhanced water wettability of the polymer after the iodine treatment.

The effects of the iodine treatment on the physical characteristics of nylon 6 have been the subject of several articles in the literature.[9-14] The formation of a new crystalline phase γ by the treatment has been shown to
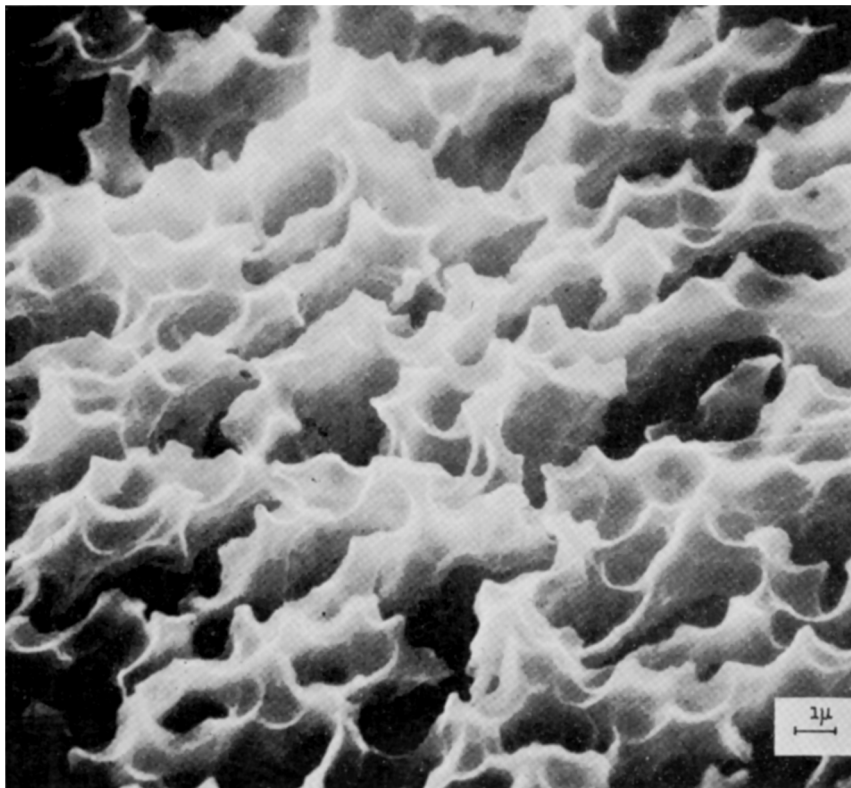
Fig. 2. Scanning electron micrograph of etched surface of polypropylene.

occur. However, the transition from the α-phase to the γ-phase has been shown to occur only under certain conditions of wash solution temperatures.[14]

The infrared spectrum of a cast nylon 6 surface shows a predominantly α-type crystallinity. If the iodine treatment is carried out and the iodine is subsequently washed at temperatures below 40°C, the surface of the nylon is predominantly of the γ-crystallinity. However, if the temperature of the wash solution is above 40°C, the resultant crystallinity of the nylon surface is α, as shown in Figure 6. Figure 7, showing the x-ray diffraction of nylon 6 surfaces, is in agreement with the infrared data.

Part (a) of Figure 7 shows that if the washing of the iodine is carried out at 80°C, essentially no crystallinity conversion is seen. However, if the washing is performed at room temperature, a conversion to the γ-crystalline phase occurs as shown in part (b) of Figure 7. This figure
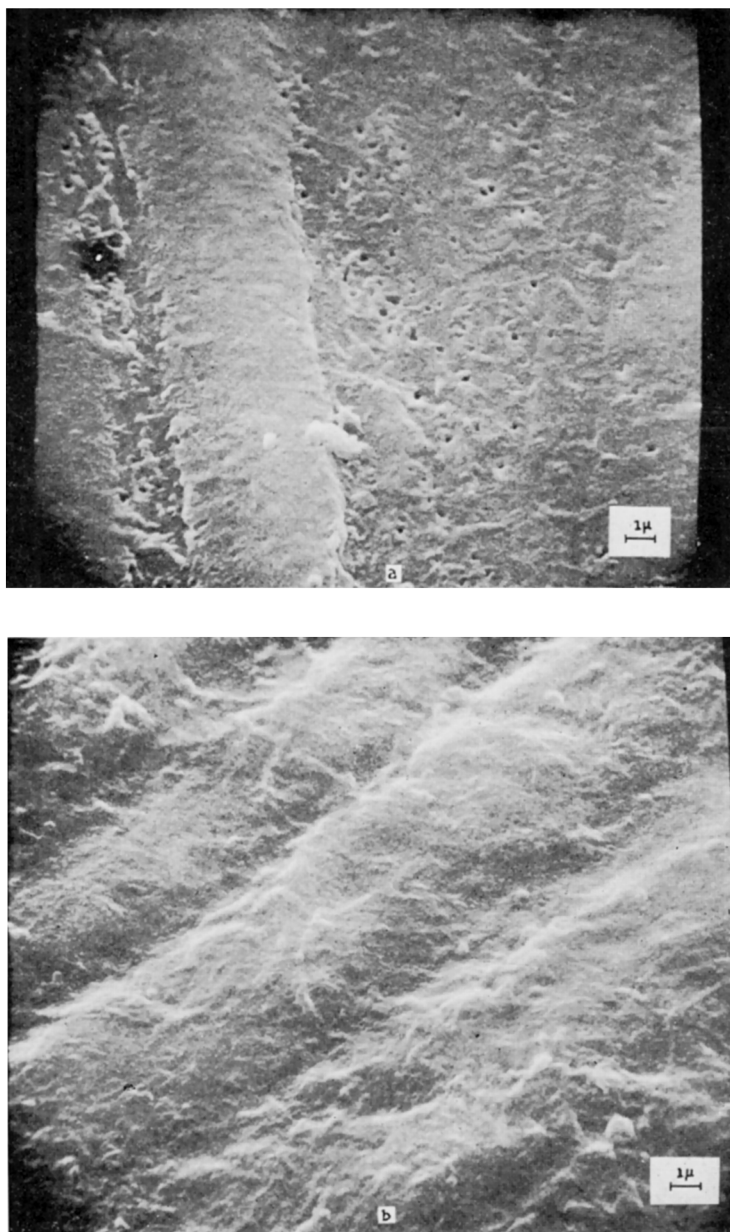

Fig. 3. Scanning electron micrographs of nylon 6 surfaces: (a) before iodine treatment; (b) after iodine treatment.
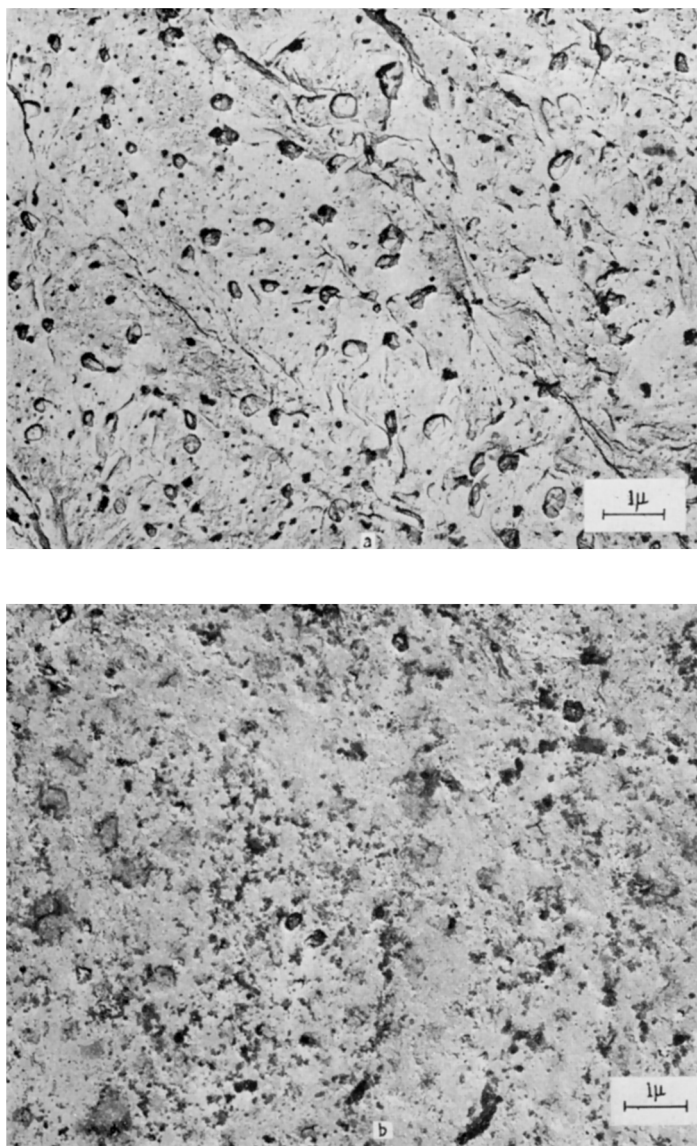
Fig. 4. Transmission electron microscope pictures of nylon 6 surfaces: (a) before iodine
treatment; (b) after iodine treatment.

depicts the diffraction pattern under a chromium source of stacked thin
films of nylon, iodine treated and washed at room temperature.

Although, under the optimum conditions of the iodine treatment of
nylon for plating, there seems to be no crystalline conversion, the overall
crystallinity of the nylon, as shown in Figure 7a, is lower after the treat-
ment.   A thorough investigation is under way to try to elucidate the effects

of the amount and type of crystallinity on the adhesion between the metal and the nylon.   A lower crystallinity at the surface leads to a softer surface and hence better penetration of the metal ions from the aqueous solutions. This will allow a better interaction of the metal with the polar nylon mole-
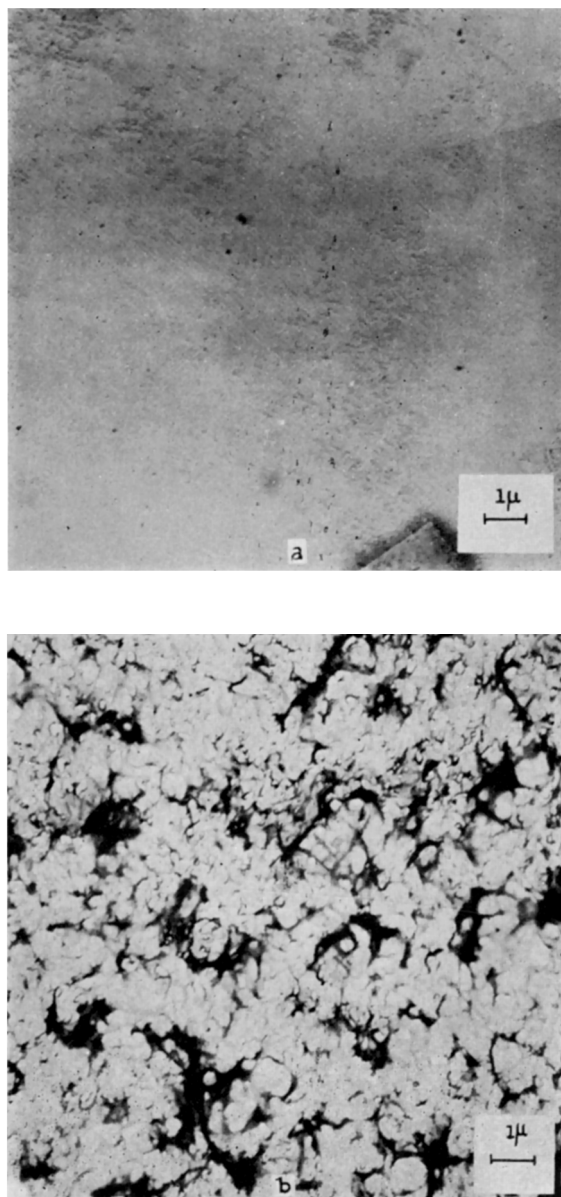

Fig. 5. Transmission electron microscope pictures of nylon 66 surfaces: (a) before iodine treatment; (b) after iodine treatment.
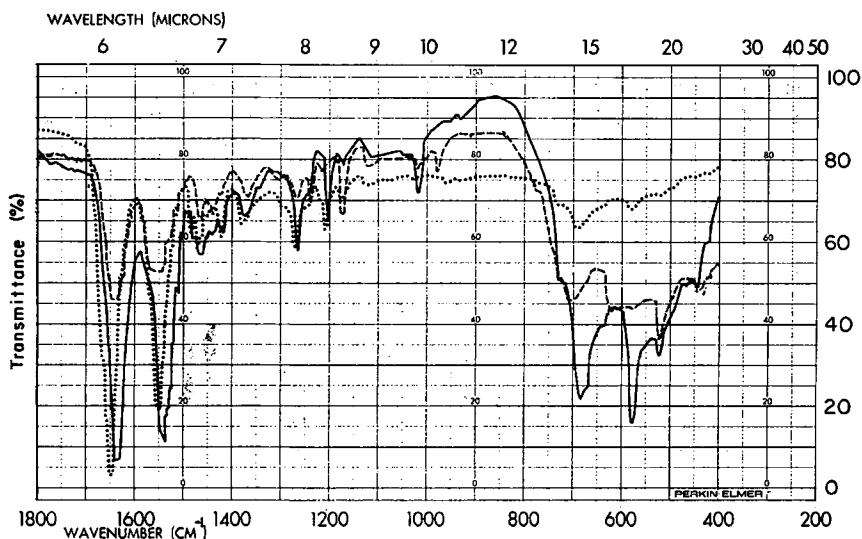
WAVELENGTH (MICRONS)

Fig. 6. Infrared spectra of nylon 6 samples: (...) cast surface untreated;   (———) I_2
treated and washed at 60°C; (- - -) I_2 treated and washed at 30°C.

cules.   Table II shows that the surface hardness of nylon 6 and nylon 66
before the treatment is higher than that after the iodine treatment.

Another important effect of the iodine treatment is that the residual
monomer and the low molecular weight polymer are washed out of the
surface of the nylon.   It was observed that when the wash solution was
cooled to room temperature, a small amount of precipitate was formed.
Infrared spectroscopy on the precipitates showed that it was in part α-
nylon 6.   Cast nylon 6 is known to contain 1–5% of the monomer and
oligomers.   Adhesion failure between the metal and the plastics has in
many instances been attributed to low molecular weight compounds on the
surface of the polymeric material.

In conclusion, this paper demonstrates that an appreciable adhesion
between electroless metal and the nylon surface is possible through iodine
treatment.   The treatment does not impart any appreciable etching to the

TABLE II
Surface Hardness of Nylon Samples

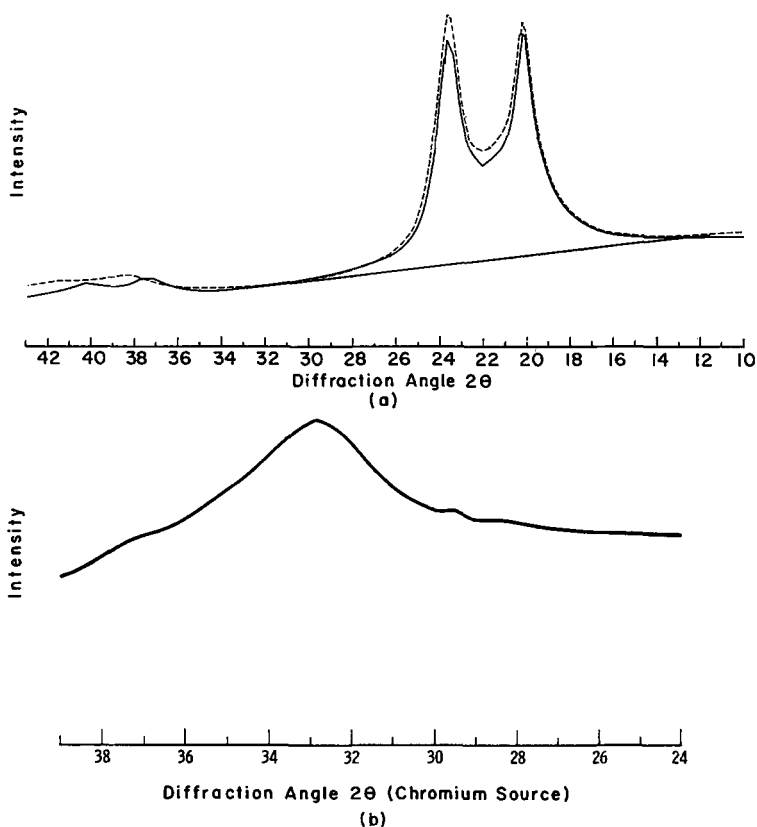|	Samples	Treatment	Knoop hardness
1.	Nylon 6	Cast, untreated	865
2.	Nylon 6, I_2 sorbed	30 sec in I_2 (R.T.), no wash	583
3.	Nylon 6, I_2 desorbed	30 sec in I_2 (R.T.), 4 min in glycol/water at 60°C	715
4.	Nylon 66	Untreated	660
5.	Nylon 6, I_2 desorbed	30 sec in I_2, 4 min in glycol/water at 60°C	418

Fig. 7. X-Ray diffraction patterns of: (a) cast nylon 6 (- -), and I₂-treated surface washed in ethylene glycol at 80°C (——); (b) nylon 6 films I₂-treated and washed in ethylene glycol at room temperature.

surface of the polymer, and therefore mechanical keying between the plastic and the deposited metal is excluded as a mechanism for adhesion. It is believed that the improved adhesion is due to factors that enhance chemical interaction of the metal with the polar groups of the nylon. A study is under way to investigate the effects of crystallinity on the metal adhesion of plated nylon.

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