TECHNICAL PAPERS

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"Plating on Plastics II"

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DECEMBER 4-5, 1968
Park Plaza Hotel
New Haven, Connecticut

DEPARTMENT OF DEFENSE
PLASTICS TECHNICAL EVALUATION CENTER
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"PLATING ON PLASTICS II"

Regional Technical Conference

Sponsored by the

Connecticut Section

Society of Plastics Engineers, Inc.

December 4 and 5, 1968

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OBJECTIVE COMPARISON OF VARIOUS PLATABLE PLASTICS SUBSTRATES FOR APPLIANCE BACKSPLASH PARTS

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and

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ABSTRACT

The General Electric Company is interested in the development of large plated plastics parts to replace plated zinc die cast parts. The plastics part is expected to give the same over-all appearance as the die casting and meet all of the performance requirements for the application.

An experimental program was developed to analyze seven plastics substrates (two ABS, four polypropylene and one impact polystyrene) all plated by commercially available plating processes. Seventeen tests were run to determine the thermal, physical and mechanical properties of each plated substrate. The results are being used as the basis for later evaluation programs by the Plastics Laboratory and the engineering test laboratories.

From an over-all performance standpoint, plated polypropylene gives better performance than plated ABS or polystyrene. The polypropylene was especially superior where high temperature and/or humidity were present. One polypropylene gave the best general performance and will be considered further for severe applications, and other substrates performed well enough to be considered for less critical applications.

The results of this program will have a broad distribution throughout the Appliance and Television Receiver Group, and could have a significant effect on the use of plated plastics in various appliances produced by the General Electric Company.

INTRODUCTION

Chrome plated accent parts have long been used in major appliances to provide the look and feel of quality. Today, the customer expects such parts as end caps, handles, trim frame edgings, knobs, push buttons and name plates to be chrome plated on all but the economy priced models. Most of these parts are being made from chrome plated zinc die castings while a few small parts are made from chrome plated plastics. As better quality platable plastics and improved plating methods become available, the appliance industry will consider changing to chrome plated plastics on more of these parts.

This paper covers the case history of a program to evaluate chrome plated plastics backsplach end caps. This is a continuing program in which plated plastics end caps are subjected to a series of tests designed to evaluate their performance in appliance environments. Although a particular large part was used, many of the tests were general enough to provide information which will be used in determining the acceptability of plated plastics for use throughout the Appliance and Television Receiver Group of the General Electric Company.

(author, modified)

THE BACKSPLASH END CAP

Every G. E. appliance with a backsplash has a cap at each end. On many models these end caps are chrome plated zinc die castings, while on others, they are ceramic coated steel. About five years ago, a particular program was initiated to replace the latter with a pigmented thermoplastic cap on some economy models. A mold was purchased and parts were molded in colors which matched the ceramic colors. Unfortunately, the parts did not have the strength, stiffness, appearance and "feel of quality" necessary for the application, so the program was dropped.

Several years later, as part of a program already underway to evaluate the use of plated plastics in appliances, we reactivated the end-cap program. It is our hope that this part (Figure 1) will be the first of many large functional parts which will change to plated plastics. To date, plated plastics are being used only on small parts such as knobs, push buttons and trim strips.

All molding and mold revisions in the program have been done at Moll Tool and Plastic Company, Evansville, Indiana. Each material in the program was molded under the supervision of a technical service representative from the material supplier and plated at a source chosen by the supplier. In this way, we assume that the plated parts submitted for test represent the best parts possible using that particular polymer in our mold. Later plans are to revise the mold and reevaluate certain polymers which performed well during this program.

Seven polymer substrates were submitted, two ABS, four polypropylene and one impact polystyrene. These substrates were plated by one or two of three commercial plating methods giving us a total of nine sample groups in the program. Initial examination of these samples revealed that the plated plastics end caps had the stiffness, appearance and "feel of quality" that the unplated end caps lacked. We also noted that there was significant cost reduction when compared to a plated zinc die casting. In this paper we will discuss tests which show other reasons for the changeover.

MATERIAL SUPPLIERS

The policy of the General Electric Company is that we do not report competitive test results to any polymer supplier. We hold this information as confidential, so we will code the name of the polymer supplier for this report.

TEST PROGRAM

The test program was designed to give an over-all picture of the performance of plated parts made from seven different polymers when subjected to the environments expected in appliance applications. Most of these tests give general results (G), while a few are designed specifically to evaluate the performance of the plated plastics end cap (p).

A. Appearance (G)

All test samples were visually examined on all surfaces to determine whether the sample could pass the following appearance requirements for production parts.

1. Appearance Surfaces - Should be bright, uniform and free from visible defects or blemishes, including:
    - a. plating voids or uneven plate,
    - b. blisters,
    - c. warpage of the substrate,
    - d. pitting,
    - e. discoloration, and
    - f. flow lines.
2. Non-Appearance Surfaces - Should not have blisters and the junction with the appearance surface should have a peel strength equal to that of the appearance surface.

B. Thermal Cycle Test (G)

The parts were subjected to the following thermal cycle:

1. heat to 180°F for one hour,
2. Place at room temperature for one hour,
3. hold at -20°F for one hour,
4. return to room temperature for one hour, and
5. repeat (1) through (4).

The parts were subjected to ten cycles and examined after each cycle for changes in appearance as outled in item (A).

C. Static Temperature Test (G)

Parts were subjected to 180°F for seven hours, cooled, examined, and then returned to 180°F for 30 days with periodic examination for appearance changes.

D. Peel Strength Test (G)

One-inch wide strips were cut from the center of the part. These samples were then chemically stripped of the chrome and nickel layers, and additional copper was plated on the existing layer. The relative peel strength was then determined using a 90° peel test apparatus in an Instron Universal Testing machine. It should be emphasized that these measurements were made on textured surfaces and may not correlate with the results from the standard peel test.

E. Plating Thickness (G)

Using standard metallographic techniques, samples were sectioned and examined using a 1000X calibrated microscope. Thickness readings were taken at several points on the textured surface of the sample and the average thickness of the inner and middle layers were determined. This technique does not allow measurement of the thin chrome layer. The textured surface of the sample prevented us from using the standard Kocour measurement technique.

F. Plate Weight (G)

The average weight of the over-all plating was determined by weighing several plated and unplated parts. This value helped us to determine the amount of plating on the nonappearance surfaces.

G. High Heat and Humidity Test (G)

Parts were placed horizontally in the vapor over a closed 180°F water bath for 30 days. One of the samples from each group had a six-inch knife cut through the plating along the front surface. The samples were examined for appearance changes (item A) and for loss of adhesion at the cut.

H. Steam Exposure Test (G)

For this test, parts were mounted vertically on a water-cooled heat sink and were sprayed for one hour with a jet of steam from a $\frac{1}{4}$-in. tube located two inches from the front surface of the end cap. The steam was then stopped for 30 minutes to allow the sample to cool before the cycle was repeated. The cycle went continuously for 30 days, and again, one sample had a knife cut on the exposed surface. The samples were examined for the same changes as noted in item (G).

I. Stiffness Test (G)

In order to determine the improvement in stiffness caused by the plating, a $1\frac{1}{2}$-in. diameter steel ball was pressed into the center of the part at a rate of 0.05 inches per minute. The end cap was mounted in a special holder designed specifically to provide support around the entire outer edge of the end cap, and the holder was mounted on an Instron Compression Load cell as shown in Figure 2.

J. Impact Test (p)

During manufacturing or installation of the appliance, it is possible that the unit could be pushed into some object. The best estimates indicate that the unit would probably be moving between one and two ft/sec. at the time of impact. We calculated that this speed could be achieved by sliding an impact sled down a 5° ramp as shown in Figures 3 and 4. In order to simulate the high force associated with the heavy appliance hitting an object, we loaded 66 lbs. on the sled. This weight traveled $5\frac{1}{2}$ inches down the 5° ramp so that the $\frac{1}{2}$-inch diameter nose was moving at about 1.7 ft/sec. at impact. The sample was mounted in the special holder discussed in item (I) and the nose impacted on the appearance surface at the center of the part. The force of impact was found using a force gauge connected to an oscilloscope.

K. Twist Test (p)

Since an assembler might twist the part during manufacture, a special fixture for the Instron was developed which twisted an end cap at 40° per minute until part fracture or yield (Figure 5).

L. Cantilever Beam Test (p)

In order to determine the relative load bearing capabilities of the various end caps, they were mounted as a cantilever beam with a two-pound weight hung from the free end. The deflection of the free end was measured at various times.

M. Gradient Temperature Test (p)

A special door was constructed in an oven so that parts could be inserted half way into the oven. The inside of the oven was at 180°F and the circulated air outside the oven was about 100°F, so the sample saw approximately an 80°F gradient. This test was designed to determine the effect of the severe thermal gradient sometimes encountered in certain applications. An additional test was run with a 250°F oven temperature to test the plated polypropylene end caps.

N. Special Tests

1. Unmolding Temperature - The temperature at which the unplated plastics end caps just begin to distort due to molded-in stress was determined.
2. Flammability - The effect of contact with an open flame was determined. This was of interest because of certain Underwriters' Laboratory requirements.
3. Electric Spark - An end cap was placed across a 120V-20 amp circuit and the effect determined.
4. Acetic Acid - Both ABS materials were immersed for two minutes in glacial acetic acid and the effect noted.

TEST RESULTS AND DISCUSSION

Each of the seven plastics will be identified in these results by a number (ABS = 1, 2: PP = 3 to 6; and PS = 7) and, where two platers were used on the same material, the samples will be designated as A and B. The tests performed in this program fell into three groups; thermal tests, mechanical tests and special tests. Before discussing the test results, we will present the results of some initial physical property examinations.

A. Physical Properties (Table I)

1. Appearance - As each group of samples was received, they were examined for over-all appearance and the presence of flaws. Six of the nine groups would have been immediately acceptable for production use while the other three were unacceptable as follows:

Group	Problem
2A	Blisters on appearance surfaces
6	Dull finish and badly warped
7	Dull finish and pitting

2. Plating Thickness - The over-all plating thickness varied widely (about .2 mils to .8 mils) on the appearance surface and was not independent of the substrate plated (Table I). There was also no consistency between the relative thickness of the inner and middle layers.

3. Plating Weight - As shown in Table I, the weights varied widely and do not correlate with the thicknesses measured. This infers that we have a varying plate thickness on the non-appearance surfaces.

4. Peel Strength - The strengths measured (Table I) were much lower than expected, especially when compared with the results reported by others.[1] Intuitively, we expected the results to be higher than those previously reported due to the added mechanical factors and increased surface area. We were particularly disappointed with the low peel test results obtained on all of the polypropylenes.

5. Unmolding Temperature - The results obtained (Table I) were typical of those expected for the materials. They show that the molded-in stresses were not high. Since the temperature requirement for plastics in some applications approaches 250°F, we see that only polypropylene materials can be considered.

6. Acetic Acid Test - The test confirmed that both ABS materials had relatively low molded-in stresses.

B. Thermal Tests (Table II)

1. Thermal Cycle Test - As shown in Table II, only one plastics material (5) completed the four or five-cycle test generally accepted in the industry. We were disappointed to find that seven of the groups failed on the first cycle and that none of the groups completed the full 10-cycle test. We should note that the material which performed well on this test performed poorly on most of the mechanical tests.

2. Static Temperature Test - All of the materials showed no effect after seven hours at 180°F while three materials failed the 30-day test. One ABS showed slight cracking and one polypropylene showed severe cracking. The pitting seen on the polystyrene sample when received increased during the test.

3. Gradient Temperature Test - Our two objectives in this test were to determine the effect of a severe gradient and to determine the heat transmission. Generally, we found the same results as in the 180°F static temperature test with the same three materials failing. However, one other material failed on this test. We were surprised to find that failures occurred in essentially the same locations as in the static test, although many of these locations were in the cooler area. The 250°F gradient test showed that some polypropylene parts could operate in a high temperature environment for long times.

   The temperature of the cold end of each end cap was determined with a contact pyrometer and was found to be 10° to 20°F above room ambient on both the 180°F and 250°F gradient tests. For comparison, we found that a zinc die casting on the 250°F gradient test would show a temperature 80°F above room ambient.

4. High Heat and Humidity - We found that the 180°F - 100% R.H. conditions failed only the ABS materials. We did see some discoloration on the surface of polypropylene samples 4 and 6, but none of the polypropylenes showed loss of plate adhesion where the plating was cut.

5. Steam Test - On this test we found both the ABS and PS materials failed by blistering and cracking on the appearance surface. Although blisters on the non-appearance surfaces are not considered failures, we did note that only one material (6) did not show these blisters.

C. <u>Mechanical Tests</u> (Table III)

The results on the mechanical tests are interesting because they allow both a comparison of the properties of the three different types of plated materials and a comparison of the improved properties gained through plating. Since all of the stiffness measurements are related to a particular test sample and setup, we have normalized all stiffness values in Table III by setting the value for zinc die castings at 100.

1. Stiffness Test - The stiffness of the ABS parts is higher than the polypropylene parts, but the improvement in stiffness due to plating is greater for the polypropylene. In fact, plating polypropylene improved the stiffness more than three times or to a point where it compared favorably with the plated ABS parts. The two polypropylene materials (4 and 5) which were plated near the thicknesses suggested

in reference 1 showed the best improvement, while the polypropylene material with the thinnest plate (3) showed the least. These tests should be done over with all materials plated to the same specification for an objective comparison.

2. Impact Test - As shown in Table III, only three of the nine plated plastics materials pass the impact test using as a failure criterion the formation of a crack on the impacted surface. The zinc die cast would also pass using this criterion, but should be considered as a failure because of the formation of an obvious dent on the surface. This is one of the potential points in favor of plastics over zinc die cast.

   As noted in the test procedure, a force gauge was used to determine peak forces due to impact. Analysis of these data show that there is an apparent interaction between peak forces and plating thickness. Additional studies are planned to evaluate the interaction before definite conclusions can be reached.

3. Twist Test - In the test, we find that plating stiffens the ABS and PP materials, but does not appear to stiffen the PS material. This lack of improvement for the PS can probably be attributed to the presence of the plating flaws (pitting) previously noted. The data also shows that the PP materials generally show a greater improvement in stiffness as a result of the plating.

   All of the materials display twist strength and angular deflection characteristics far in excess of those that would be encountered in handling or assembly. In other applications where larger deformations and loadings could occur, the plated PP samples would be favored.

   Examination of the parts after some had been twisted as much as 360° revealed that the integrity of the plating on the polypropylene parts was generally better than on parts made from the other materials. The plating on the textured surface showed less tendency to crack or peel than on the non-textured surfaces.

4. Cantilever Beam Test - For load-bearing applications where creep could be a problem, the higher modulus of the plated ABS materials would be advantageous. The test did not show a definite relationship for a particular substrate between creep and plating thickness.

D. Special Tests

1. Flammability - We found that both ABS and PP plated parts would be considered non-burning on the U.L. Subject 94 flame test for self-extinguishing materials. However, if the flame is applied for 10 or 20 seconds longer, the plastics inside the plate melts, breaks through the plate, and

ignites. This flame usually extinguishes in 30 seconds or less. If an intense flame source is used, such as a propane torch, it takes about 45 seconds to cause the sample to ignite.

2. Electric Spark - A sample was placed across a 120V-20 amp circuit. We found that the plating at the contact points burns away very fast leaving a dead system which did not ignite.

3. Dent - Using the stiffness test equipment, the ball was slowly pushed into a zinc die cast sample and an ABS sample. We found that an obvious dent can be seen when the ball has penetrated the zinc part only about 0.05 inches, while an ABS part did not even show a slight dent until past 0.25 inches. We did not run this test on the other two materials.

CONCLUSION

From an over-all performance standpoint, plated polypropylene materials appear to show better performance than the plated ABS or polystyrene materials. Polypropylene parts gave superior performance in tests where high temperature and/or humidity were present, and essentially equal performance to ABS on all mechanical tests except creep.

Based on the results of these tests, polypropylene (4) performed best and will be considered further for severe applications. For less critical applications, other polypropylene or ABS materials could be considered but would have to be evaluated against the specific application requirements. Unless the polystyrene material can be plated without pitting, we do not see any need for further testing.

It has been apparent throughout our analysis of the test results that plating thickness had a large effect on test results. Our attempts to evaluate this effect were hindered by the inconsistent quality of the plating. We also noted that the varying thickness of the plating on the non-appearance surface had an effect on test results. In future work, we plan to specify and measure the plating thickness on both surfaces.

We concluded that significant work must be done before we would consider using large plated plastics parts in production. In particular, there must be further modification to the mold and tight control will be exercised on all future molding and plating. In this way, we will be able to evaluate the available substrates as well as compare the commercial plating processes.

In future test work, we will modify certain tests, particularly the mechanical tests, in order to obtain a correlation between the test results and actual end use conditions. From these tests, we will select the material that will meet the performance standards required for the application. Extensive Test Laboratory studies will then be run to determine whether the part will perform satisfactorily in actual field usage.

ACKNOWLEDGMENT

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REFERENCE

1. Innes, W. P.; Grunwald, J.J.; D'Ottavio, E.D.; Toller, W.H., and Carmichael, C., "Chromium Plated ABS and Polypropylene Plastics - Performance in Typical Tests", August 1968.

TABLE I

PHYSICAL PROPERTIES

Sample Number	1A	1B	2A	2B	3	4	5	6	7	Zinc
Material	ABS	ABS	ABS	ABS	PP	PP	PP	PP	PS	Die Cast
Plating Thickness (Inches x 10^{-6})										
Inner Layer	630	480	460	290	120	600	550	190	570	180
Middle Layer	270	80	220	140	90	80	70	120	210	640
Plating Weight (Grams)	9.3	6.4	8.3	6.6	5.1	7.3	12.9	6.2	9.0	-
Peel Strength (Pounds per inch) (of) (sample width)	9	7	4	4	9	8	3	10+	9.5	-
Unmolding Temp. Substrate (°F)	190	190	185	185	305	305	320	305	185	-

TABLE II

THERMAL TESTS

Sample Number Material	1A ABS	1B ABS	2A ABS	2B ABS	3 PP	4 PP	5 PP	6 PP	7 PS	Zinc Die Cast
Thermal Cycle Test										
a) Cycles to 1st failure	1	1	1	1	1	3	6	1	1	>10
b) Type of failure	Cracks & blisters	Blisters	Blisters	Cracks	Cracks, blisters, peeling	Cracks	Blisters	Cracks	Cracks & pitting	No effect
c) Over-all appearance after 10 cycles	Poor	Poor	Poor	Poor	Poor	Average	Good	Fair	Poor	Excellent
Static Temp. Test										
a) Effect of 7 hrs. @ 180°F	No effect	No effect	No effect	No effect	No effect	No effect	No effect	No effect	No effect	No effect
b) Effect of 30 days @ 180°F	Slight cracking	No effect	No effect	No effect	Severe cracking	No effect	No effect	No effect	Severe pitting	No effect
c) Over-all appearance after 30-day test	Fair	Good	Good	Good	Poor	Good	Good	Good	Poor	Good
Gradient Temp. Test										
a) Effect = 180°-100° gradient	Blisters	No effect	Blisters	No effect	Cracking	No effect	No effect	No effect	Blisters	
b) Effect = 250°-110° gradient	-	-	-	-	Cracking	No effect	-	Severe blistering	-	No change
High Heat & Humidity Test										
a) Effect of cut	Plate lifting	Plate lifting	Plate lifting	Plate lifting	No effect	No effect	-	No effect	No effect	-
b) Over-all performance	Poor	Poor	Poor	Poor	Good	Good	-	Good	Good	-
Steam Test										
a) Effect of cut	Started blisters	Started blisters	Started blisters	Started blisters	No effect	No effect	No effect	No effect	Started blisters	-
b) Over-all performance	Poor	Poor	Poor	Poor	Good	Good	Good	Good	Poor	-

TABLE III

MECHANICAL TESTS

Sample Number Material	1A ABS	1B ABS	2A ABS	2B ABS	3 PP	4 PP	5 PP	6 PP	7 PS	Zinc Die Cast
Stiffness Test										
Relative Stiffness*										
Plated	12.0	7.6	13.3	10.4	7.1	9.5	12.3	6.6	6.6	100
Unplated	7.6	7.6	8.1	8.1	3.8	2.8	2.3	3.3	5.7	-
Impact Test										
Effect of impact force	Pass	Fail	Fail	Pass	Fail	Pass	Fail	Fail	Fail	Pass
Twist Test										
First strength loss (lbs.) @ deflection (deg.)										
Plated	41@50	36@44	35@44	41@48	64@128	48@166	33@44	56@96	24@40	233@52
Unplated	64@120	64@120	83@168	83@168	42@128	33@132	72@186	40@132	55@168	-
Relative twist stiffness*										
Plated	20.0	20.0	21.0	20.0	15.7	12.6	15.7	12.6	8.4	100
Unplated	11.5	11.5	11.5	11.5	6.3	5.3	8.3	5.3	8.5	-
Integrity of plate	Poor	Good	Poor	Poor	Avg.	Good	Fair	Good	Good	Very good
Cantilever Beam Test										
Deflection in one day (inches)	.36	.28	.26	.27	.99	.85	.72	.67	.39	-
Deflection in three days (inches)	.41	.35	.34	.36	Max.**	1.1	.88	.82	.48	-
Final deflection (30 days) (inches)	.63	.59	.51	.61	Max.	Max.	Max.	Max.	Max.	-

*All relative values based on zinc die castings equal to 100.

**Max. denotes that the sample deflected until the front edge touched the test frame.

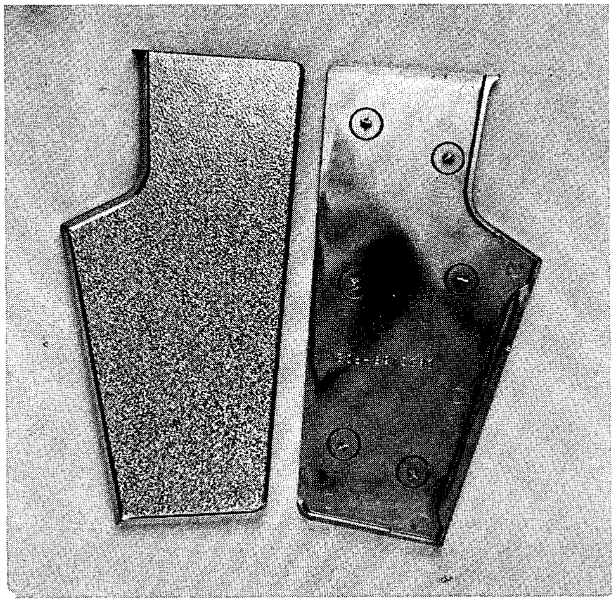


FIGURE 1

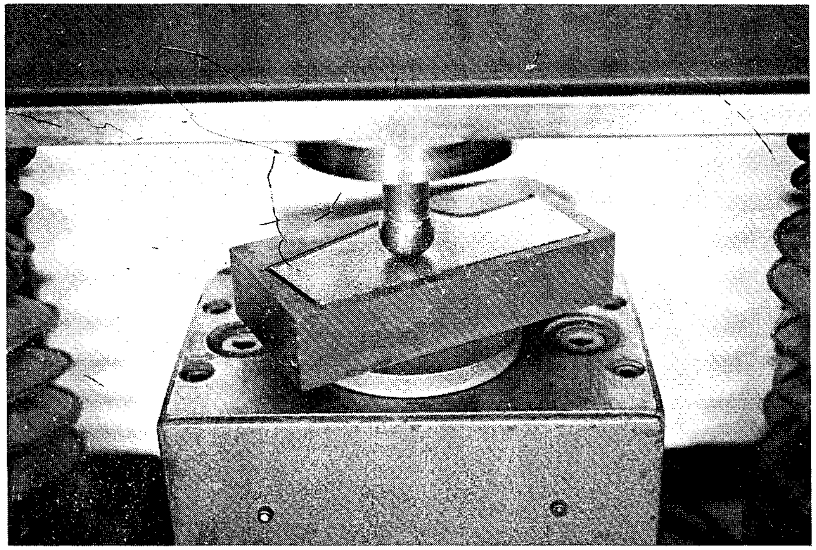


FIGURE 2

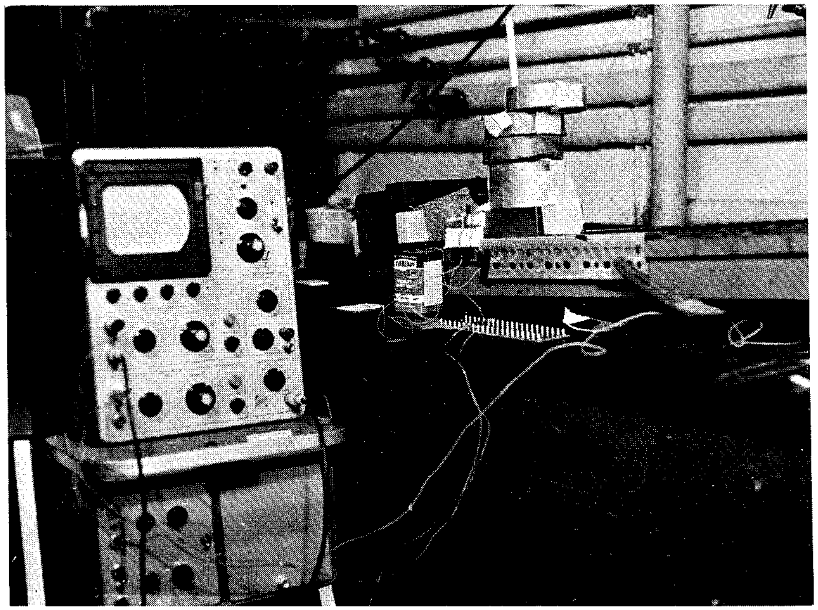


FIGURE 3

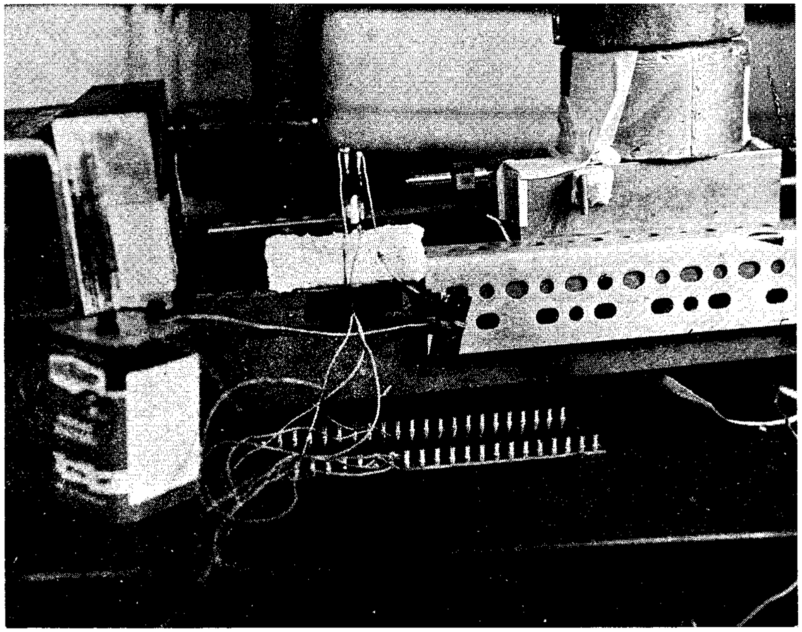


FIGURE 4

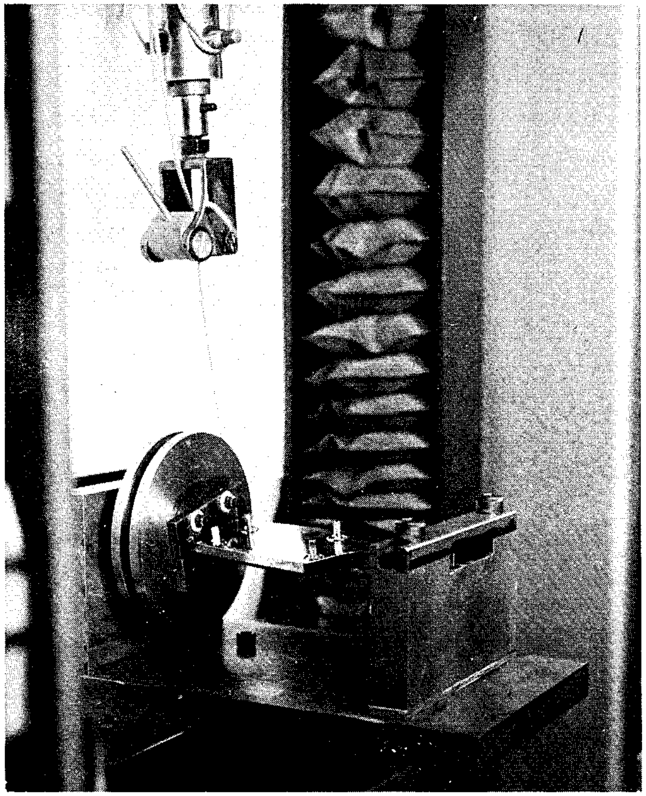


FIGURE 5

-02

MOLDING AND QUALITY ANALYSIS OF POLYPROPYLENE SUBSTRATES

Evan B. Ewan

Avisun Corp.

Marcus Hook, Pa.

INTRODUCTION

Electroplated plastics is one of the newest and most exciting areas where plastics challenge markets previously available only to metals. Although the use of electroplated plastics is only a few years old, advantages in cost, quality and performance are already evident. The recent development of a plateable polypropylene represents the second major step toward further penetration in this market. Plated polypropylene promises even greater economies and performance than heretofore available.

This paper ~~alerts the reader to~~ discusses the various factors which must be considered to produce a superior plated polypropylene part. As the title implies, The effect of processing conditions on the plateability of the molded part is discussed. Also, attention is given to an equally important factor - part and mold design considerations for polypropylene. Without a properly designed part and mold, the best molding conditions could be meaningless.

WHY POLYPROPYLENE?

There are many advantages to be obtained from plated polypropylene. Table I helps define the reasons for the increasing enthusiasm for this material. First, economics of polypropylene are more favorable than ABS. ABS will be used for comparison since it is currently utilized in the majority ofplating applications and, until now, has exhibited the best plateability and performance of the plastics available.

The lower density of polypropylene combined with the lower resin price reduces the material cost to less than one cent per cubic inch, compared to one and one-half cents per cubic inch for ABS. Improvements in molding costs, due to decreased cycle time, are also likely with many parts. Plating costs, on the other hand, are slightly higher than for ABS. As plating technology for polypropylene advances, as polypropylene resins improve, and as commercialization of plated polypropylene expands, plating costs are expected to approach those of ABS.

Quality is also an important factor, where substantial physical property improvements of the plated part can be realized. The stiffness, as shown by flexural modulus, is almost 50 per cent higher for plated polypropylene than for plated ABS. Another remarkable improvement is that of deflection temperature or heat distortion; tests at both 66 and 264 psi show no failure until the melting point of the polypropylene is exceeded (345°F).

Another important characteristic of polypropylene is its extremely low water absorption compared to other plateable plastics. This makes polypropylene a prime candidate for applications where water and steam are prevalent.

Peel strength values show that the metal-to-polypropylene adhesion is much greater than with ABS, thus eliminating the chance of blistering or peeling of the coating. Values in excess of 50 lbs./in. are being obtained consistently on commercial parts, although adhesion in the 20-30 lb. range are more common. Thermal cycling characteristics are superior with polypropylene. Normally, both ABS and polypropylene will pass standard thermal cycling tests with CuNiCr. Polypropylene is also acceptable using a NiNiCr system, while ABS is not. Due to the higher adhesion of polypropylene, thermal cycling failures are less noticeable; only hairline cracks result with no blistering or peeling of the coating.

KNOW THE PRODUCT

The introduction of a new product must be accompanied by a rapid dissemination of technical data describing its physical properties, design considerations, and the processing conditions needed to produce the best possible end results. A comparison of both similarities and differences between the new material and the current product is essential to avoid misapplication, faulty design, or incorrect processing conditions. One of the problems facing the material supplier, as he introduces plateable polypropylene, is that he is entering a market which has been dominated by ABS. When designing and molding for plating, the ABS technology is foremost in the mind of the user; and although there are many similarities, there are significant differences between ABS and polypropylene, and they must not be overlooked.

PART AND MOLD DESIGN

In order to get some exposure to polypropylene, a customer will often wish to evaluate this material in his shop, using a part currently molded or plated in ABS. This, he feels, will give him a good comparison between the two resins. Unfortunately the use of an ABS tool could result in a faulty evaluation. First, the dimensions of the part will be different because polypropylene has a higher shrinkage factor than ABS. Additionally, the higher shrinkage of polypropylene may create sink marks in areas where they were not apparent in ABS. Normally, with proper mold design, the polypropylene part could also be molded sink free. Such changes as thinner ribs, modified bosses and heavy sections, and the use of uniform wall thicknesses will eliminate objectionable sinks. A brief description of some of the critical design criteria is shown in Table II.

Secondly, ABS molds are normally designed with smaller gates and runner systems than those recommended for plateable polypropylene. The use of small gates tends to build up unnecessary stresses in the plastics. As with ABS, the stressed areas do not plate readily; and consequently low adhesion values or even blisters or skips may result. The gates can be opened thereby reducing internal stresses, although molders are not usually willing to modify their mold when evaluating a new resin. The best approach, when seeking a fair comparison, is to select an obsolete mold and allow a polypropylene supplier's Engineering Design Group to suggest modifications. Only after these changes have been completed is the mold ready for the evaluation.

MOLDING FOR PLATING

The key to molding for plating is to mold stress-free parts. Areas where surface stresses are high will not readily accept the electroplate. Since this is also true for ABS, there is a great deal of similarity between the conditions recommended for polypropylene and ABS. There are, however, some major differences between molding conventional polypropylenes and molding the electroplateable grades. Conventional polypropylene is usually molded under conditions where a high degree of packing is obtained. This eliminates sinks and provides a better looking part. These conditions may leave some stresses in the part, but this is usually unimportant, as polypropylene does not stress crack. Another word of caution before proceeding with the discussion on actual molding conditions - no mold release agents such as silicones or zinc stearate powders should be used if the part is to be electroplated.

A number of test programs have been run in an effort to determine the effect of molding conditions on the plateability of polypropylene. These studies have used both plaques and molded parts, and have included such variables as melt temperature, mold temperature, cycle time, injection speed, and injection pressure. Parts have been plated with heavy copper plate for adhesion values and copper/nickel/chrome and nickel/nickel/chrome for thermal cycling and for appearance. Although no single particular program produced all of the desired answers, logical conclusions were developed from the combined data. The bulk of the available data is on adhesion values using 1.5 to 2.0 mils of copper. At the time of this writing definitive conclusions on the effect of molding conditions on thermal cycling are unavailable. Available data indicate, however, that there seems to be no good relation between thermal cycling and adhesion for polypropylene. Parts having adhesion of around 20 lbs./in. may pass thermal cycling requirements, whereas parts with high adhesion (40-50 lbs./in.) may not. Of course, if adhesion values are low (less than 5 lbs./in.), blistering can occur with thermal cycling. Polypropylene adhesion, however, is normally high enough to prevent blistering or peeling should a hair-line crack occur. Other types of plastics do depend on adhesion to pass thermal cycling.

For the purpose of comparison, the data presented utilizes adhesion values as the criteria for determining the plateability of the substrate. Figure 1 shows the effect of melt temperature on the adhesion. Data developed on both screw and ram machines are also shown. Screw presses normally produce better results. Generally speaking, adhesion increases as melt temperature increases. Normally, a low temperature melt is more difficult to push through the machine and, consequently, will create a greater amount of internal stress in the part. Although we have insufficient data, we have seen some evidence that under certain conditions a reduction in adhesion may occur at very high melt temperatures. Since the effect of melt temperature is a substantial factor, medium to medium-high melt temperatures are preferred for plating.

Figure 2 shows that the effect of mold temperature on the adhesion of polypropylene is very modest. There is a general increase in adhesion with increasing mold temperature, although there is only a six to seven unit difference over the entire range tested. This low response to mold temperature is very important in utilizing polypropylene, as lower mold temperatures can be helpful in molding sink-free parts. With ABS, the use of a cold mold cannot normally be tolerated as stress cracking of the part may occur as it passes through the plating solutions. Polypropylene does not stress crack; consequently, this is not a problem.

Figure 3 shows the effect of cycle time on adhesion. As with mold temperature, the curve is relatively flat, indicating that cycle time has very little effect on plateability. We have seen a somewhat greater reduction in adhesion when extremely short cycles have been used. When using more conventional cycles, cycle time does not have a significant effect on plateability.

Figure 4 shows that the effect of injection speed on adhesion is the most critical of the molding parameters. A fast ram speed, which would normally be used for polypropylene, is very detrimental for plating. Adhesion values are expected to increase by as many as twenty units when going from a fast to a slow ram. Using a slow ram speed the shear and internal stresses are reduced and the part readily accepts plating.

Figure 5 shows the effect of the injection pressure on adhesion. Here again, the high injection pressures normally used for polypropylene are not recommended when the part is to be plated. The use of a lower injection pressure will reduce the stresses and provide a more readily plateable substrate.

A comparison between molding conditions normally recommended for conventional polypropylene, for electroplating grade polypropylene, and for ABS is shown in Table III. Since molding for plating is aimed at reducing stress levels and molding for conventional polypropylene is designed to produce the best sink-free appearance part, compromises are often necessary. For plating, the slow ram should always be used. Variations from the normally recommended melt temperature and injection pressure can often be used without severely reducing the plateability of the part.

Since molding economics depend on regrinding runner systems, etc., a study has been made to determine the effect of regrinding on both the polymer and the plateability. Table IV shows that there is no significant change in the polymer or the adhesion of the coating after three 100 per cent regrinds.

POST MOLDING TREATMENT

With polypropylene, an annealing operation can be used to relieve highly stressed parts and thus render them plateable. This post-treatment operation should be considered as a method of salvaging otherwise unusable parts, and should not be considered as part of the routine molding and electroplating process. Annealing of the surface and not the entire body of the part will produce satisfactory results. Oven annealing does a very adequate job - 250°F for 15-30 minutes is usually sufficient. This is a much lower annealing temperature than would normally be used to completely stress relieve polypropylene. Other methods which will anneal only the outer skin of the part are also quite effective and can often be accomplished in less time.

TESTING FOR STRESSES

In order to provide a quality control test for molded parts efforts have been made to develop a test which will detect stressed areas. Since polypropylene does not stress crack, the use of chemicals such as acetic acid to detect stress in ABS is ruled out.

A NEW TYPE OF POLYPROPYLENE "ON THE WAY"

All of the preceding information has dealt with commercially available electroplating grades of polypropylene. Because of the effect molding conditions have on plateability of plastics, there has been a major effort to develop a polypropylene that would be less sensitive to molding variables. A great deal of progress has been made and a new type of plateable polypropylene is currently being field tested as an experimental product. This new resin not only appears to plate well over a wider range of the molding conditions, but etches at reduced times and temperatures, and has outstanding thermal cycling and high temperature properties. Parts have been tested up to 270°F without failure of the plating.

Although we do not expect this new resin to be a cure-all, we feel it represents the type of progress which is continually being made in the new field of electroplating grade polypropylenes.

SUMMARY

Electroplateable polypropylene offers a great many advantages over other types of electroplating grade plastics on the market today. Both better economy and better quality, particularly in metal-to-plastics adhesion, thermal cycling characteristics, high temperature durability, and low water absorption are commanding more attention for this new material.

The production of superior electroplated polypropylene parts depends on both proper part and mold design and the selection of proper processing conditions. Mold design considerations include elimination of potential sink areas which would impair appearance. Equally important is the use of large gates and runner systems to minimize the development of stresses in the molded part. It is suggested that the design group of a polypropylene manufacturer be contacted for design suggestions before metal is cut for the mold. Corrections are always easier and less expensive to make on the print.

Molding conditions which minimize stresses produce the best plateability. These are not the same conditions normally used for molding conventional polypropylene, therefore, some compromises are often necessary. Molding conditions having the greatest beneficial effect on plateability are slow injection time, medium to medium-high melt temperature, and low injection pressure.

Annealing of highly stressed unplateable polypropylene parts will render them plateable.

New and better grades of plateable polypropylene are on the way. These will be relatively insensitive to molding conditions, plate at lower temperatures and less time, and have better performance than materials commercially available today.

ACKNOWLEDGMENTS

The author wishes to thank Avisun personnel in both Basic Research and Sales Service for their efforts in the development of these data, and those from Mac Dermid and Enthone for plating many of the samples and to draw these conclusions.

BIBLIOGRAPHY

1. Narcus, Dr. H., "Recent Developments in the Field of Plating on Plastics", SPE Technical Paper, Volume XIV (pp. 246-248).

2. Versaw, W. D., "Keys to the Profitability Production of Plated Plastics Parts", SPE Technical Paper, Volume XIV (pp. 249-254).

3. Steen, S.S., "Molding ABS for Electroplating", SPE Technical Paper, Volume XIV (pp. 255-262).

4. Innes, W. P., Grunwald, J.J., D'Ottavio, E.D., Toller, W.H., and Carmichael, C., "Chromium Plated ABS and Polypropylene Plastics - Performance and Typical Tests", presented at the 1968 AES.

TABLE I

COMPARISON BETWEEN ELECTROPLATING GRADES OF ABS AND POLYPROPYLENES

	ABS	Polypropylene
Economics:		
Material Cost		
Density	1.07	0.95
Cost, per lbs.	40¢ range	28¢
Cost, per cubic inch	1.50¢	0.96¢
Cost, per sq. ft. of area[1]	20¢	13¢
Molding Cost (due to improved cycle time)	-	Slightly lower
Plating Cost	-	Slightly higher
Total Part Cost	-	Lower
Quality:		
Physical Properties of Plated Parts		
Tensile yield strength @ 2"/min., psi	7300	5400
Tensile modulus @ 2"/min., psi	600,000	420,000
Flexural modulus, psi	900,000	1,320,000
Deflection temperature @		
66 psi, °F	214	N.F.[2]
264 psi, °F	-	N.F.[2]
Performance of Plated Parts		
Adhesion, 2 mil copper, lb/in.	10-15	20-50
Thermal cycling, CuNiCr	Normally acceptable	Normally acceptable
NiNiCr	Not normally acceptable	Normally acceptable

[1] Assuming the typical part has two sq.ft. of area per lb. of resin.

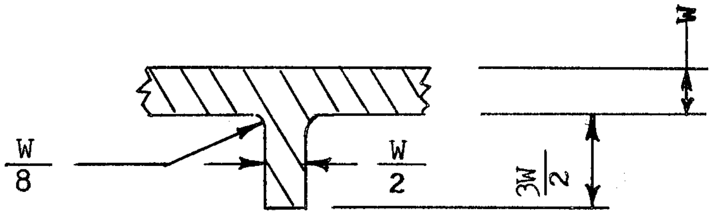
[2] Specimen did not deflect until the polypropylene melt point (345°F) was exceeded.

TABLE II

MOLD AND PART DESIGN CONSIDERATIONS

I. Part Design

A. Rib Design

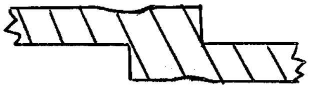


B. Boss Design

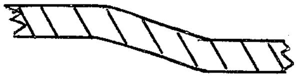
1. Relocate on non-appearance surfaces
2. Redesign to reduce material mass
3. Mask sink marks by surface texturing

C. Wall Thickness

1. Wall thickness should be as uniform as possible

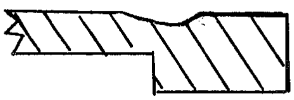


unsatisfactory



satisfactory

2. When varying wall thicknesses are necessary, the transition should be as smooth as possible.



unsatisfactory

satisfactory

D. Areas to avoid when designing a part for plating

1. Parting lines on appearance surfaces
2. Sharp corners
3. Blind holes and deep recesses
4. Highly raised lettering or texturing
5. Ribs or slots too closely spaced
6. Failure to provide an adequate place to rack the part.

II. Gate and Runner Design

A. Gates

1. Gates should be larger than normally recommended for polypropylene. Gate diameter should be 100%-80% as large as the thickest wall of the part.
2. Smaller, self-shearing, gates can be used on relatively small parts such as knobs.
3. Gate should be located in the thickest section of the part.

B. Runners

1. Runners should be full round or trapezoidal.
2. Runners feeding gates should never be smaller than .250"-.300" in diameter, or less than the thickest section of the part.

C. Area to avoid when designing a mold for plateable parts

1. Parting lines, knock-out pins, and gates on appearance surfaces.
2. Too little draft on walls.

TABLE III

SUGGESTED MOLDING CONDITIONS

	ABS	Polypropylene		
	Plateable Grades	General Purpose	Plateable Grades	*
Melt Temperature	High 460-510°F	Low-Medium 400-450°F[1]	Medium 420-450°F[1]	2
Mold Temperature	Medium-High	Low-Medium 50-120°F	Medium 90-120°F	4
Cycle Time	As required	As required	As required, but avoid very short cycles	5
Injection Speed	Slow	Fast	Slow	1
Injection Pressure	Low	High (15-20,000 psi)	Low (10-12,000 psi)	3

*Order of decreasing effect on plating adhesion for polypropylene.

[1] Melt temperatures for screw machines. When using ram press, increase melt temperatures by about 50°F.

TABLE IV

REGRIND STUDY ON ELECTROPLATING GRADE POLYPROPYLENE

	Virgin Pellets	Virgin Part	First Regrind	Second Regrind	Third Regrind
Flow rate, gms/10 min.	6.0	7.3	8.1	9.0	10.9
Shrinkage (in./in.)	--	.022	.021	.023	.023
Tensile yield strength @ 2 in./min., psi	--	4300	4300	4350	4350
Tensile impact, ft.lbs./sq.in.	--	37	42	40	43
Izod impact, ft.lbs./in. (notch)	--	.38	.33	.30	.33
Flexural modulus, psi	--	165,000	159,000	165,000	173,000
Heat distortion, 66 psi	--	94°C	95°C	88°C	95°C
Adhesion (2 mils of copper) lb./in. of water	--	27	29	26	25

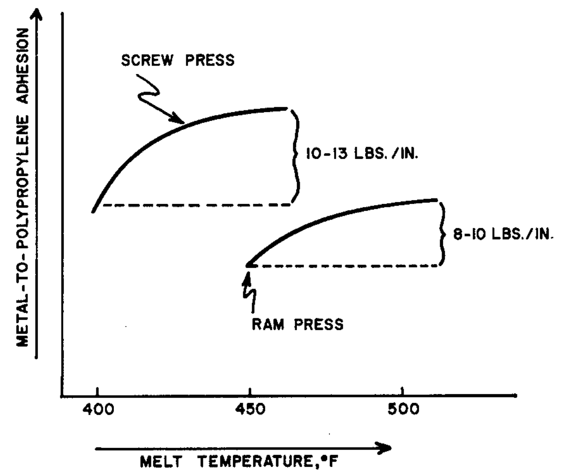


FIGURE 1: Effect of melt temperature on the metal-to-plastic adhesion for electroplating grade polypropylene.

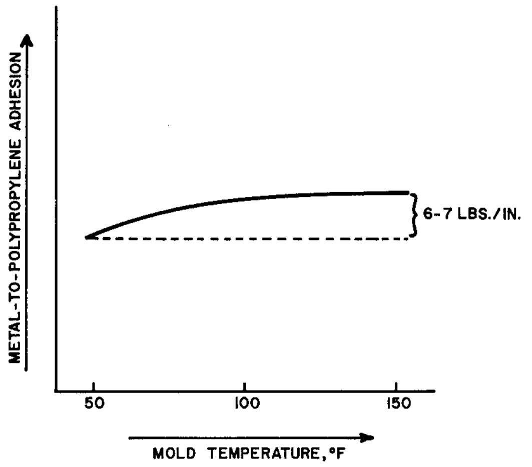


FIGURE 2: Effect of mold temperature on the metal-to-plastic adhesion of electroplating grade polypropylene.

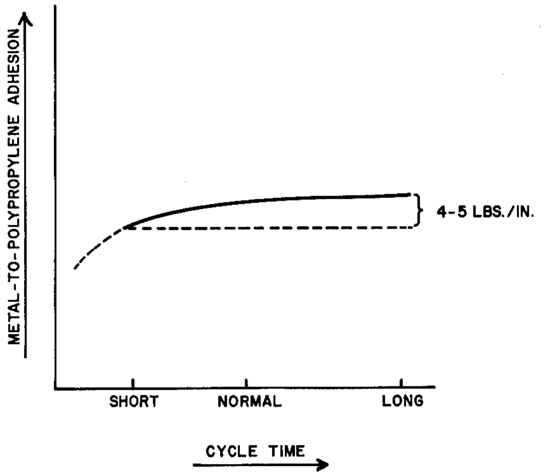


FIGURE 3: Effect of cycle time (overall) on the metal-to-plastic adhesion of electroplating grade polypropylene

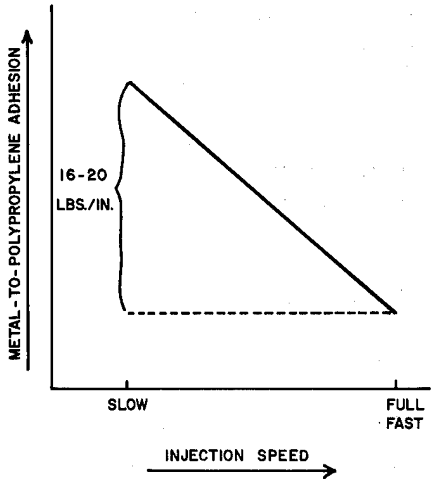


FIGURE 4: Effect of injection speed on the metal-to-plastic adhesion of electroplating grade polypropylene.

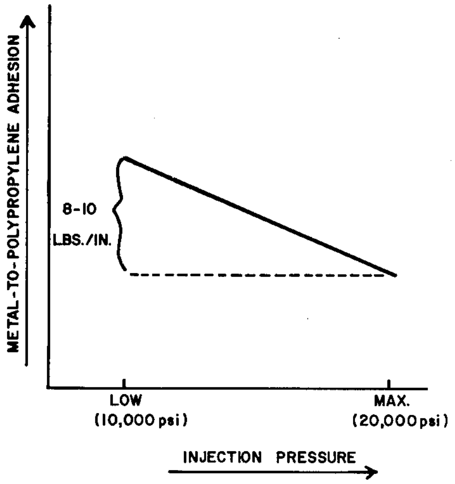


FIGURE 5: Effect of injection pressure on the metal-to-plastic adhesion of electroplating grade polypropylene.

03

MOLDING AND QUALITY ANALYSIS OF ABS SUBSTRATES

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INTRODUCTION

Electroplated plastics is a rapidly growing field. It is one in which both the molder and plater can exert numerous controls on a finished part. In this field, ABS is used more extensively than any other plastics.

This paper describes the advantages of ABS and tells what the molder can do to produce a quality ABS substrate. It takes into consideration economics, processing conditions and quality control in screw machine molding.

Cauther)

ADVANTAGES OF ABS

A. Economics

Many types of plateable plastics, other than ABS, are commercially available. Of these, polypropylene appears to have drawn the most attention. On this basis, much literature has been presented concerning the price of polypropylene vs. ABS. In order to examine the economics of ABS, we will draw a similar comparison between these materials.

1. Material and Molding Costs

Table I shows the costs of materials and molding. ABS is priced at 40 cents per pound and has a specific gravity of 1.07. The modified plating grade of polypropylene has a specific gravity of 0.98 and is priced at 28 cents per pound. For unmodified resins best values are obtained using those resins priced at 29 cents per pound with a specific gravity of 0.91. Table I summarizes these costs for a one-square-ft. panel 1/8-in. thick.

2. Plating Chemicals Cost

Table II shows the chemical costs involved in plating our sample panel. Conservatively, preplate chemicals alone for ABS cost about 15 cents per square ft., including five cents for the etch or conditioner. For modified polypropylene a conditioner costing about seven cents per square ft. is substituted for the conventional ABS conditioner. However, for unmodified polypropylene, a special conditioner costing approximately five cents per square foot is added to the conventional ABS preplate system. Electroplating chemicals will cost another 10 cents per square foot. Applying a typical factor for overhead, manufacturing and profit to materials, the average plater can be expected to charge:

75¢/sq.ft. - ABS
81¢/sq.ft. - Modified polypropylene
90¢/sq.ft. - Unmodified polypropylene

Table III brings these values into proper perspective. On the basis of these data all three materials are competitive, costwise. Modified polypropylene costs 1.5 per cent less than ABS while unmodified polypropylene costs 6.5 per cent more.

B. Material Properties

Table IV shows the typical properties of plating grade ABS. Presently, adhesion values for ABS are in the 12-15 lb./in. strip width range, however, indications are that new and better ABS materials, with adhesion values in the 20-25 lbs. range, will soon be available.

Note the Rockwell hardness of ABS. This relatively high value makes ABS less susceptible to scratching before plating and marring after plating, as opposed to a softer material.

ABS has a linear mold shrinkage of 0.004 in./in. This low value is desirable. Materials with a high mold shrinkage are more likely to have surface sink marks which become magnified when plated.

Impact strength is another area in which ABS excels. In addition to having high impact values at room temperature, it possesses good cold temperature impact.

ABS has a high flex strength and flexural modulus. It also has high heat distortion temperatures at both 66 and 264 psi fiber stress. These properties combine to make ABS less prone to flexing or distortion under rack contact tension, especially at elevated temperatures. Materials not possessing this rack stability will deform in hot plating solutions, and have this deformation permanently encapsulated by subsequent electroplating.

ABS is amorphous, and, therefore, lacks a sharp freezing point. It is deliberately molded at a slow fill rate into a hold mold to produce a dimensionally stable, low stress part. Crystalline materials possess a relatively sharp freezing point. Stresses introduced during processing become locked into the molded part. When immersed into hot conditioners and electroplating solutions, these materials readily warp as molded-in stresses are relieved. This is one of many situations where the advantage of producing a low stress part offsets the slightly longer cycle time necessary to do so.

CONCLUSION

By changing the proportions of its three ingredients, ABS can be adapted to do an infinite number of demanding jobs. Combining extreme versatility with good economics and excellent properties makes ABS a good bet to remain the undisputed leader in the field of electroplated plastics.

PROCESSING CONDITIONS

A. Stock Temperature

Figure 1 shows the effect of stock temperature on strip adhesion. At a slow injection speed (11 second fill time), adhesion showed a 5.2 lb. increase for a value at 530°F stock temperature, as opposed to 350°F. Adhesion values continue to increase with stock temperature up to the point where degradation sets in. At this point adhesion values fall sharply.

B. Cylinder Residence Time

Quite often low adhesion values are obtained due to an improper balance between machine shot size and cylinder capacity. Figure II illustrate this point. Notice the 3.8 lb. decrease in adhesion of shot number five as compared to shot number one. This loss is attributed to a slight degradation which occurs as the material sits in the cylinder. Lowering the stock temperature would reduce this degradation. However, strip adhesion values for the earlier shots would be lower. The best solution is to use a smaller machine. The optimum ratio of machine capacity to shot size varies with material, cycle and screw design. In this particular case the ratio should be no greater than three to one.

C. Mold Temperature

The influence of mold temperature is displayed in Figure 3. There is a 0.6 lb. increase in adhesion upon decreasing the mold temperature from 180°F to 90°F. However, splay marks become evident at mold temperatures below 110°F. This points out that optimum mold temperature is a compromise between maximum adhesion and suitable appearance.

D. Dwell Time (Injection Hold Time)

Figure IV shows that ram dwell time has no practical effect on adhesion. Using a slow fill time of 10 seconds, dwell times of one, six and eleven seconds yielded similar results. It should be pointed out that extrapolating this curve in either direction will yield unfavorable results. Zero dwell time will show deformation at the gate due to flow-back of material. Extended dwell time would lead to excessive cycles and eventually material degradation.

E. Injection Speed

The effects of injection speed on adhesion are relatively well known in the plating industry. Figure 5 displays our results. Here it is interesting to note the large increase in adhesion when going from a fill time of five to 10 seconds, as opposed to the near zero change in going from two to five seconds. This indicates that molded-in stresses began to dissipate above a five-second fill time.

F. Injection Pressure

Excessive injection pressures introduce molded-in stress. Figure 6 shows a 0.8 lb. decrease in adhesion when going from a minimum fill pressure (MFP) plus 50 psi to a minimum fill pressure plus 200 psi. Adhesion values obtained for injection pressures greater than MFP + 250 psi were inconsistent. However, they were all on the low side. These low values constitute the dashed section of the curve.

G. Annealing Effects

It is well known in the plating industry that annealing before testing increases strip adhesion. But what are the times and temperatures involved? Figure 7 provides some interesting information. Here it is seen that annealing at room temperature (72°F ± 1°F, 50 per cent R.H.) for 25 or more hours produces adhesion values equivalent to those obtained on samples annealed two or more hours at 180°F. Furthermore, it shows that annealing increased the adhesion by 1.5 lbs. This increase is attributed to the elimination of molded-in stress.

QUALITY CONTROL BY MEANS OF THE ACETIC ACID TEST

It is the job of the molder to provide the plater with a quality substrate. One of the main criteria in producing a quality ABS part is minimizing molded-in stress. The acetic acid test is an accurate means for locating stress concentration areas in molded ABS parts. The test consists of immersing the molded part, at room temperature in glacial acetic acid for three minutes. After immersion, the part is thoroughly rinsed and then dried in air. At this point, the surface is examined at 50X magnification. Two types of surface may be seen: a highly stressed whitened surface and a low-stressed uniform, non-whitened surface. The highly stressed areas show one or more of the following irregularities: scratches, channels, oblong pits, and mottled etch. These irregularities as well as a low stressed surface, are shown in Figure 8. The high stress situations are undesirable. Particular attention should be given to the gate areas. All of the irregularities mentioned should be eliminated since they will have an adverse effect on the finished part. Specifically, areas which are stressed will give low adhesion values as compared to non-stressed parts. Secondly, areas of stress will not etch at the same rate as non-stressed areas. This difference in etching will lead to non-uniformity in plate adhesion.

Notice the uniform etch pattern created by the acetic acid in the low stressed piece - this is desirable. It shows that there is no stress concentration present and indicates that uniform etching will take place during plating.

The quick, accurate stress check, afforded by the acetic acid test will yield a more economic process for both molder and plater. Working together they can establish a quality control process which is mutually satisfactory. The end result will be better quality at lower cost.

BIBLIOGRAPHY

1. Schwartz, E. and Hartley, J. C., "The Acetic Acid Test - Useful Tool for Stress Control and Plating Quality", SPE JOURNAL, March 1967.

TABLE I

	ABS	Modified PP	Unmodified PP
Material	$ 0.28	$ 0.19	$ 0.17
Molding	$ 0.25	$ 0.19	$ 0.19

Based on sample panel 1' x 1' x 1/8".

TABLE II

	ABS	Modified PP	Unmodified PP
Preplate Chem.	$ 0.15	$ 0.17	$ 0.20
Electroplating Chem.	$ 0.10	$ 0.10	$ 0.10
Total Chem. Cost	$ 0.25/sq.ft.	$ 0.27/sq.ft.	$ 0.90/sq.ft.
Plating Price (Including a typical cost factor)	$ 0.75/sq.ft.	$ 0.81/sq.ft.	$ 0.90/sq.ft.

TABLE III

	ABS	Modified PP	Unmodified PP
Material	$ 0.28	$ 0.19	$ 0.17
Molding	$ 0.25	$ 0.19	$ 0.19
Plating	$ 1.50	$ 1.62	$ 1.80
Total Price/Panel	$ 2.03	$ 2.00	$ 2.16

TABLE IV

PROPERTIES OF ABS

Adhesion (lbs/in. Strip Width)	12-15 lbs
Hardness, Rockwell	108
Mold (linear) shrinkage (in/M)	0.004
Impact strength	
(ft-lbs/in. - notch) 73°F	4.2
(1/2" x 1/8" bar) 20°F	1.5
Flex. strength (psi)	8,500
Flex. modulus (psi x 103)	280
HDT 264 psi (°F)	203
66 psi (°F)	210
Tensile strength (psi) (0.25"/min.)	6,000
Tensile modulus (psi x 10^3)	310

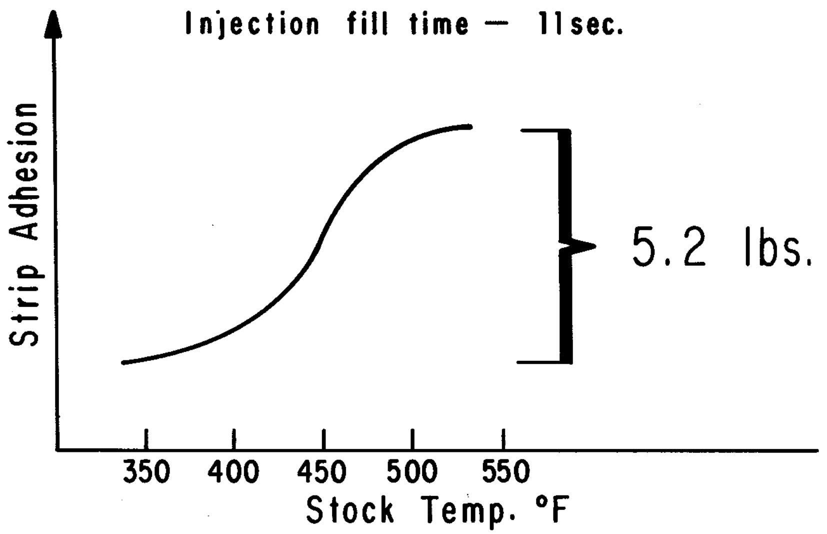


FIGURE 1

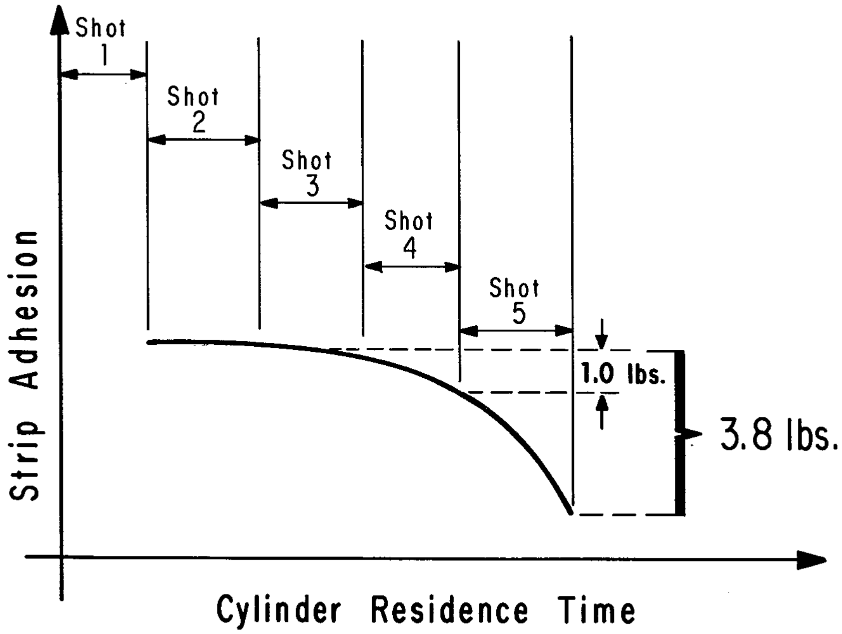


FIGURE 2

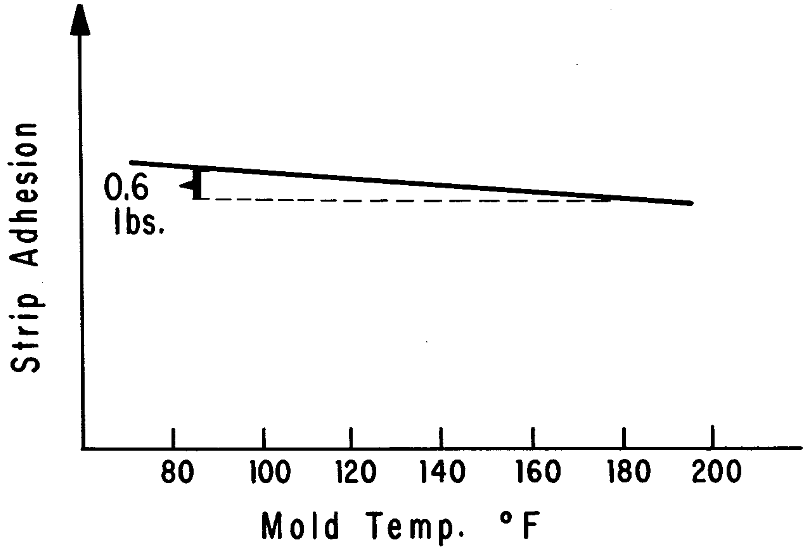


FIGURE 3

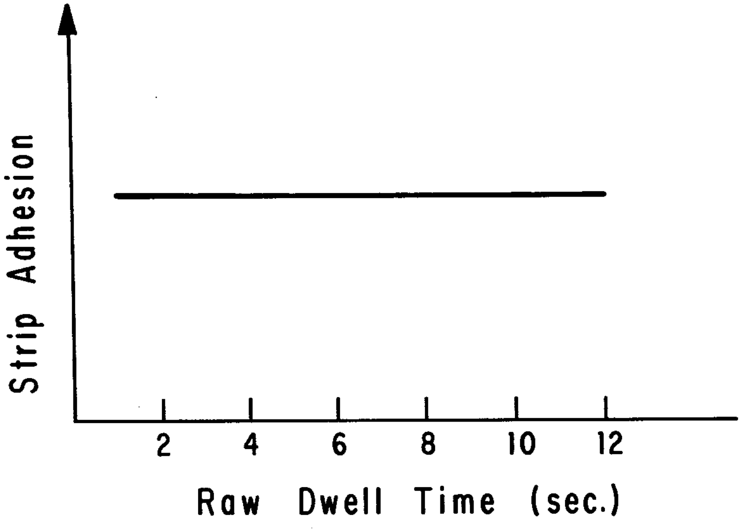


FIGURE 4

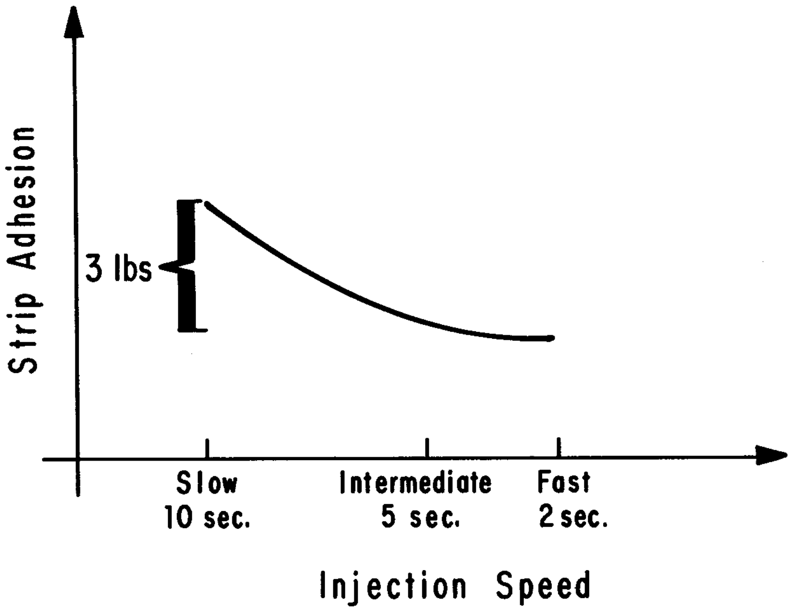


FIGURE 5

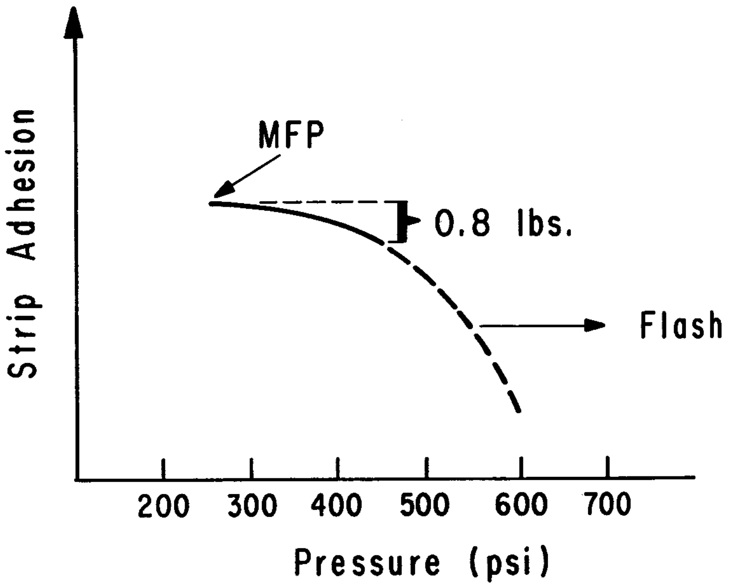


FIGURE 6

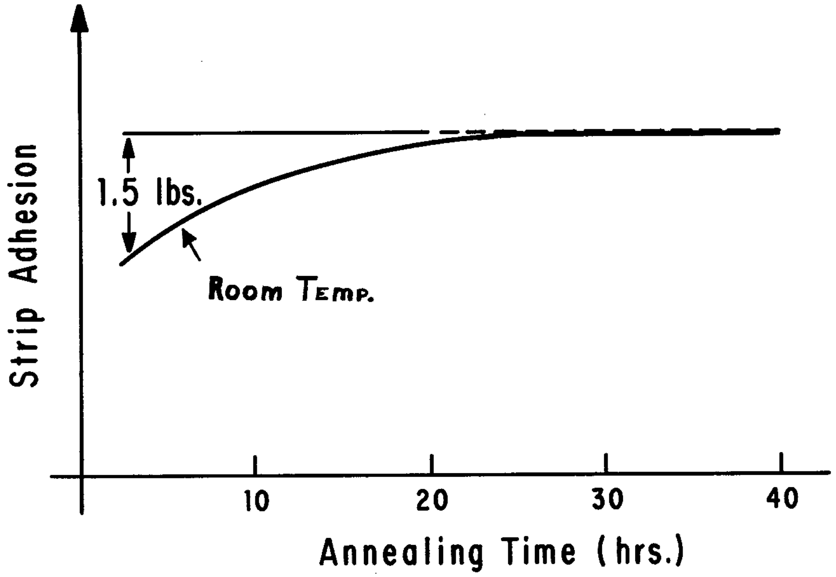
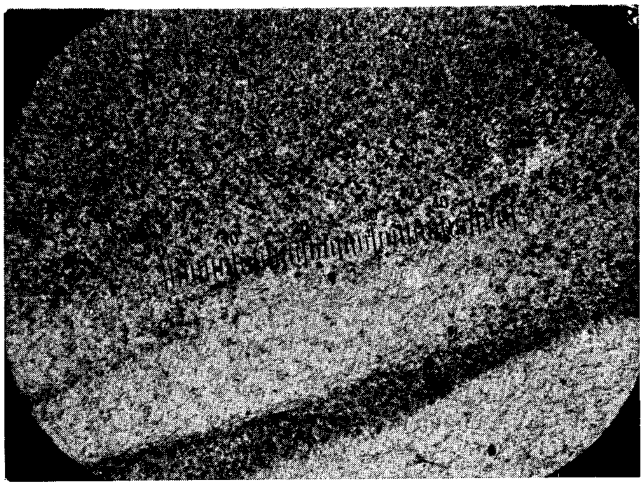
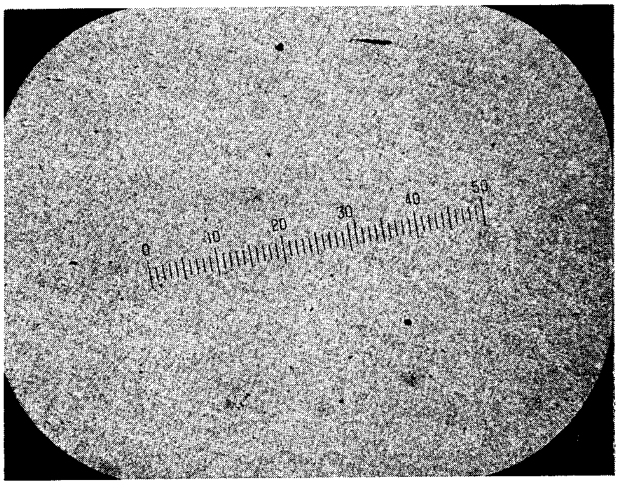


FIGURE 7

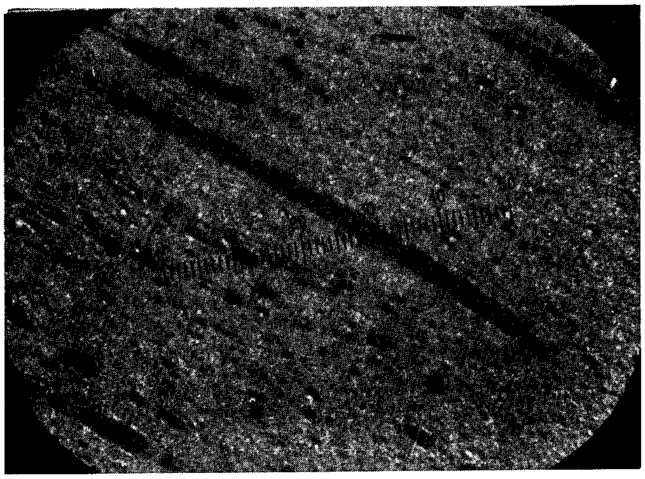
High Stress
Mottled Etch



Low Stress
Uniform Etch



High Stress
Pits & Channels



High Stress
Scratches

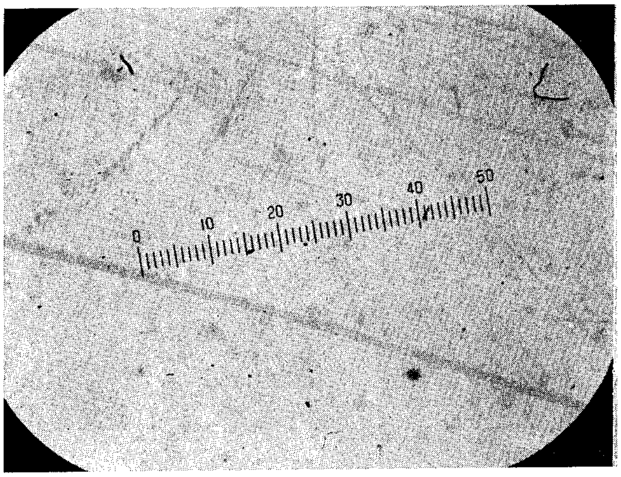


FIGURE 8

PREPLATE SYSTEMS

Charles R. Shipley, Jr.

Shipley Co., Inc.

"Preplating" is the connecting link between plastics and the metal electroplate. Preplating provides the adhesion of the metal to plastics, and renders the plastics conductive so that electroplating can be performed. Thus preplating is the "heart" of plated plastics.

Overly simplified, preplating is accomplished by three major steps:

1. conditioning plastics surfaces for adhesion,
2. seeding the plastics with catalytic particles,
3. electroless metal plating to provide conductivity.

These steps produce deposits of adherent conductive electroless metal. Metal is then electroplated to the desired thickness and finish. The finished product exhibits strong adhesion between the plastics and the metal electroplate, with the preplating as the connecting link.

Adhesion values vary for different plastics, and for different preplate systems. Under laboratory conditions bond strengths exceeding 12 lbs. have been reported on at least 10 different plastics. However, as of September 1968, only ABS is being plated in significant quantities with repetitive success under large volume production conditions. Until now polypropylene plating results have been promising but inconsistent while polysulfone is being plated with good success in small quantities.

Treatment of plastics is predicated upon the plastics material, molding conditions, configuration of the part, electroplate composite required and thermal cycle requirements. The level of adhesion obtained governs the latitude available under the above conditions with current polymers. While many plastics plating systems are now being used commercially with success, it is imperative that the preplate system be selected for specific end-use products, the requirements for which are well within the capabilities of the particular preplate system. Also, the choice of the plastics should be predicated upon the end-use of the plated plastics object.

CONDITIONING PLASTICS SURFACES

Typical conditioning methods are these:

1. Mechanical abrasion (or equivalent)
2. Etching of the plastics, as with chromic acid
3. Selective leaching

4. Chemical solvation of the plastics
5. Combinations of the above

A. Mechanical Abrasion

For most work mechanical abrasion is not acceptable because the adhesion is minimal. But in the case of small objects which can be successfully plated by encapsulation techniques, mechanical abrading produces fully acceptable results. These applications include buttons, curtain rings, radio push-buttons and the like. The encapsulation system has been used for many, many years. Since this art is well known in the industry, I will devote my paper to the new art of plating directly onto plastics with strong adhesion - the needs for which are so great and so varied.

B. Chromic Acid Etching

Chromic acid etching of plastics is the most commonly used method for conditioning plastics for preplate adhesion. In the case of ABS, chromic acid etching by itself prepares the plastics suitably for most applications in use today. However, there are limitations to chemical etching as the sole step in conditioning plastics for preplate adhesion. For example, in the case of ABS only a few so-designated "plating grades" can be successfully plated, and the molding tolerances are very stringent even for these grades. Uniform consistency and predictability of results have caused manufacturing problems and have curtailed the types of plastics parts being plated. However, where chromic acid etching is properly utilized and where proper controls are maintained over the molding and plating steps, ABS plating has proved to be successful, even for fully automatic plating lines.

The "chromic acid" solutions vary considerably in formulation and even in the method of etching the plastics. Generally, these solutions must be formulated for the specific plastics to be plated, and must be compatible with the particular plastics plating system.

C. Leaching

Leaching of the substrate is successfully used for plating directly onto ceramics, but to my knowledge the leaching method is not being used for conditioning plastics. Leaching is accomplished by the selective dissolution of a constituent in the substrate, and, therefore, affords adhesion that is essentially mechanical by creating anchor points. In the case of ABS butadiene is etched rapidly by chromic acid, and so part of the resultant adhesion might be due to a leaching action since the acrylonitrile and styrene constituents are attacked only to a small extent.

D. Chemical Solvation

Chemical solvation is now being used for conditioning plastics, not as a single step, but as a pretreatment step prior to chromic acid treatment. This dual-step conditioning method has immense possibilities for plating plastics. For example, polysulfone is successfully plated by a dual-step conditioning method employing a solvent step. Chemical solvation serves to remove or attack the plastics by solvent action. The glazed surface is penetrated, rendering the plastics less chemically resistant and more susceptible to chromic acid etching. This pretreatment can make it possible to utilize less powerful chromic acid solutions and thereby provide greater operating tolerance and reproducibility.

Conversely, unless the chemical solvation bath is properly formulated, the preconditioning can create ruinous results, such as distorted design configurations and swollen parts containing excess residual solvent.

In summary, the common similarity among various plastics conditioning methods is that the plastics is attacked to a controlled extent, in order to afford anchor points for mechanical bonding and/or to produce chemical bonding. The solutions must be carefully formulated, properly mixed with chemicals of acceptable purity, and then properly controlled - in order to achieve good bonding with repeatable results.

SEEDING THE PLASTICS

Seeding the plastics with catalytic particles is not a routine step in plating plastics, as has been inferred by the fact that nearly all technical literature concerning plating on plastics discuss plastics conditioning or electroless deposition or bonding mechanisms, but do not discuss seeding in detail. The facts are that the seeding method can favorably affect adhesion strength, and that improper seeding methods can cause "star-dusting", an appearance defect sometimes occurring in bright decorative plating. While not conclusively proved, seeding methods can also directly affect corrosion resistance of ABS plated parts.

Seeding is the key to plating non-conductive surfaces, since electroless metal is deposited only on surfaces which are seeded with catalytic particles. These particles initiate the electroless metal deposition. This very function points up the obvious conclusion that seeding affects adhesion since uniformity and density of adsorbed catalytic sites necessarily improve adhesion. Unevenness of adsorbed catalytic particles adversely affects adhesion and plating appearance, and furthermore can cause plating irregularities which result in corrosion resistance weak spots. Inadequate seeding causes voids in the metal plate. Seeding systems are essentially of two types:

1. a two-step method in which a catalytic metal is reduced in situ on the plastics,

2. a patented colloidal method in which pre-reduced catalytic metal particles are adsorbed in the pores of the plastics.

A two-step method generally employs an acidic stannous chloride solution followed by a palladium chloride solution. In step one, stannous ions are first adsorbed in the pores of the plastics, then at step two these stannous ions serve to reduce palladium in situ on the plastics surface.

The colloidal method employs an acidic bath of pre-reduced colloidal palladium. These colloidal particles are so finely divided that they will pass safely through a five-micron filter. The particles, which literally are moving at fantastic rates of speed, bombard the plastics surfaces and are adsorbed in tiny pores. After treatment in this colloidal catalyst bath, the work is generally treated in an accelerator solution.

While both systems are successfully used, the colloidal method has found the greater commercial acceptance for plating ABS. Handbook formulations for the two-step system might cause "star-dusting", and so should be thoroughly tested before production use.

DIFFERENCES BETWEEN ELECTROLESS COPPER AND ELECTROLESS NICKEL AS A CONDUCTIVE BASE FOR ELECTROPLATING

For decorative plating on plastics nearly all platers at the present time use electroless nickel-phosphorus or electroless copper as the conductive base for electroplating. In view of this I will confine this comparison to these two electroless metals, although other electroless metals such as nickel-boron can be used successfully.

A strange contradiction exists concerning conductivity: electroless nickel deposits are only about two per cent as conductive as electroless copper, yet a lesser thickness of nickel will suffice than for copper! The reason for this is that thin electroless copper has a tendency to "burn off" in electroplating baths at the time when current is applied for electroplating, whereas most electroless nickels in adequate thickness do not burn off.

Complete electroplate coverage occurs rapidly over electroless copper, whereas the electroplate coverage creeps slowly across the electroless nickel starting from the contact points and filling in as the electrodeposits become sufficiently conductive. On small and moderate-sized parts complete electroplate coverage over the electroless nickel is usually accomplished within 60 seconds. However, in the case of parts requiring more than a minute for complete coverage, the delayed coverage with acid copper electroplate will destroy adhesion values which cannot be detected until after testing is completed. To prevent such a problem an electrolytic nickel strike bath is now being used by most plastics platers.

A few years ago it was reported that electroless nickel permitted non-plating on plastisol-coated racks, thus eliminating the costly step of re-racking. This is only partially true. Non-plating on racks is governed by the preplate system in addition to the plating characteristics of the electroless metal bath. When a suitable preplate system is employed, most electroless nickel baths will not plate on the racks whereas electroless copper baths need to be specially formulated to prevent plating the racks.

With respect to adhesion contradictory reports are prevalent that nickel produces better adhesion than copper, and that copper produces better adhesion than nickel! Neither is the case. However, it is true that adhesion differences do exist, but the differences are not due to whether the deposit is nickel or copper. Differences are due to the preplate system used. Some preplate systems work better with nickel, others with copper, but not necessarily with one or the other since the properties of the electroless metal deposition bath can strongly influence the adhesion results. It is a fact that both electroless nickel and electroless copper serve as excellent bases for adhesion.

Corrosion resistance is still another subject in dispute. As a metal, electroless nickel-phosphorus has exceptional corrosion resistance properties; copper does not. As to be expected, the nickel-chrome electroplating finishes generally govern the corrosion resistance of the plated object when an effective preplate system is employed; however, a good electroplating system will not assure corrosion resistance if the preplate system is substandard. In exterior atmospheric tests, both electroless nickel and electroless copper have proved to be acceptable.

A major advantage of electroless copper is the reliability of bonding between copper and electroplate finishes. Nickel-phosphorus becomes passive upon standing, thus creating severe activation problems whereas none exist with copper. However, proprietary electroless nickel baths are now available which have eliminated the passivity problem.

Electroless nickel has two major advantages over copper. First of all, nickel deposits as thin as 10 to 15 millionths of an inch are practical for large volume operation. Copper deposits must be heavier, thus increasing costs and increasing deposition time. Fast electroless coppers offset the time advantage, but there is a tendency for fast coppers to cause roughness in electroplating or to sacrifice some adhesion strength between the plastics and the metal plate. The second major advantage of nickel is bath potlife. However, proprietary electroless copper baths are now available which have long potlife when used regularly, and which possess excellent stability.

For articles that are selectively plated, it is easier to use electroless copper, since the unwanted copper can be easily removed by mild etching solutions. However, with suitable techniques nickel-phosphorus is successfully used for selective plating.

Of course, there are major differences in the chemical composition of electroless nickel and electroless copper. Electroless nickel-phosphorus baths utilize hypophosphite as the reducing agent, and, for decorative plating of plastics, are generally operated at a pH between seven and 10 and at temperatures from 70°F to 120°F, depending upon the bath formulation. Electroless copper baths utilize formaldehyde as the reducing agent, and are generally operated at a pH between 11 and 13, and at temperatures between 65°F and 80°F.

Aside from decorative plating applications the choice between copper and nickel depends upon the functional application. For printed circuits electroless copper is used almost exclusively as a base for subsequent electroplating. The recent development of heavy ductile electroless coppers will bring about the widespread manufacture of additive circuits whereby the copper conductors will be selectively electroless copper plated to full thickness directly onto the plastics substrate, thus eliminating copper electroplating.

For magnetic tape, electroless nickel-cobalt alloy is plated directly onto a plastics substrate, usually Mylar, or a non-magnetic nickel-phosphorus is plated on the plastics prior to electroplating a magnetic metal alloy. Also, there are applications where electroless nickel-phosphorus is plated to full thickness directly onto glass-reinforced plastics in order to provide hardness and wear resistance.

FUTURE PREDICTIONS

Looking ahead, we can now safely predict that most plastics will become "plateable" including: polystyrene, polycarbonate, polyphenylene oxide (PPO), polyaryl ether, epoxy, and other electronic grade plastics.

Also, we can foresee many advances in the plating of plastics - especially in the reliability of preplate systems. Within a few years, the plating of many plastics will become commonplace and even routine.

05

PREPLATE SYSTEMS FOR POLYPROPYLENE

E. B. Saubestre

Enthone, Inc.

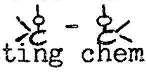
BONDING OF METALS TO PLASTICS

The exact manner in which metals adhere to plastics is not yet known, despite the large volume of plated plastics parts being produced commercially today. This is yet another example of the plater's art outdistancing theory. Nonetheless, a number of preliminary theories have been offered and most of them may be said to fall into two broad categories: mechanical and chemical.

A. Mechanical Theory

According to this theory, conditioners and etchants serve to create an extensive network of fine, shallow, pits on the surface of the plastics. Many photomicrographs have been published which illustrate this effect. It is further postulated that the acid selectively attacks certain chemical constituents in the surface layer more than others so that the resulting pits are of such a shape as to promote an "anchoring" effect for subsequent electrodeposits. There is little doubt that such surface configuration promotes the adhesion of metals to plastics. On the other hand, it would appear that mechanical effects alone cannot account for the very high values of adhesion obtained when proper bonds are formed between metals and plastics. A proper bond is one such that in Jacquet (or pull) testing, the failure occurs inside the plastics and not at the metal-plastics interface, i.e., there is cohesive failure of the plastics before there is adhesive failure of the metal-plastics interface. It is a bit difficult to see how purely mechanical bonding alone could account for this.

B. Chemical Theory

According to this theory, conditioners and etchants serve to create chemical bonds between plastics and metal. This theory has never been proved definitively, but several authors have given indirect evidence supporting it. Consider, for example, the $>C = C<$ bond, which is often found in the surface of thermoplastic materials. This bond is relatively easily oxidized to the following:  $>\overset{\overset{|}{O}}{C} - \overset{\overset{|}{O}}{C}<$. The latter offers unsatisfied oxygen linkages, permitting chemical bonding of some other material to the polymer structure. That this concept is not the sole criterion for adhesion is shown by the fact that, for a given chemical system, adhesion is still affected by surface roughness and other factors.

C. Comparison of ABS and Polypropylene

The typical surface of an ABS plastics contains many double-bonded carbons as a result of the butadiene content. Thus, ABS lends itself well to surface oxidation treatments. It is worthy of note that, depending upon molding conditions, the surface of ABS plastics may be rich in SAN content (which contains less butadiene) and that such surfaces are comparatively harder to condition. By comparison, polypropylene surfaces contain much lower amounts of double-bonded carbons. Hence, polypropylene surfaces are much less susceptible to chemical oxidation treatments than ABS. This is the basis for the difference between the conditioning or etching of polypropylene and ABS.

CONDITIONING OF POLYPROPYLENE

With the above in mind, then, conditioners and etchants for polypropylene will be discussed under two categories.

A. Mechanical Bonding

Since polypropylene is relatively difficult to oxidize, the use of purely mechanical bonding is popular. In such cases, the surface is attacked by an etchant which generally tends to form an extensive crack pattern. This network of cracks provides an excellent way to "anchor" subsequent electrodeposits to the polypropylene surface. In order to provide the proper network of "anchoring" sites, however, relatively high temperatures are required in the etching step.

B. Chemical Bonding

There are several approaches to obtaining good chemical bonding of metals to polypropylene. One is to copolymerize the polypropylene with readily oxidizable materials. An elementary example would be to add butadiene, but more sophisticated approaches are also used. Thus, polypropylene surfaces so treated could be conditioned somewhat like ABS surfaces. Another approach is to irradiate the polypropylene to cause a sufficient degradation as to produce available unsatisfied bonding sites for subsequent chemical bonding in the conditioning step. Yet another approach is to apply a coating to the surface of polypropylene which contains oxidizable groups. For example, a coating could be applied which contains a high percentage of double-bonded carbon to make the surface respond somewhat like an ABS surface. In general, when ordinarily difficultly oxidizable surfaces are given such coatings, they should be extremely easy to oxidize in view of their relative thinness in most cases. For example, the oxidizability of the $>C = C<$ bond can be enhanced by conjugating it, that is, by alternating single- and double-bonded carbons: $-c=c-c=c-c=$.

C. Polypropylene Conditioners

The best conditioners and etchants found to date for developing desired "anchoring" networks for mechanical bonding or for oxidizing surfaces to provide chemical bonding all contain chromic acid as the basic oxidizer in a strongly acidic medium, although there are rather wide variations in other constituents present. While some proprietary products exist, no further information is currently available. As a general rule, compared to ABS, polypropylene surfaces seem to be rather more sensitive to the exact composition and operating conditions of the conditioner. Commonly, temperatures used in achieving either type of bonding are high, generally about 180-190°F. The use of such high temperatures presents the latent problem of possible distortion of the part, especially if it is racked under stressed conditions during the etching period. Factors such as time of immersion and concentration of conditioner vary with molding conditions, exactly as in the case of ABS, and it is difficult at present to give any general guides.

ELECTROLESS PLATING OF POLYPROPYLENE

It is evident from the foregoing that once the polypropylene surface has been properly conditioned, the surface may then be treated virtually as an ABS surface through subsequent processing. Thus, properly conditioned polypropylene surfaces may be electroless plated by any of the three major methods now in use on ABS surfaces.

1. Sensitize in tine salt	1. Catalyze in tin sol	1. Activate in catalytic salt
2. Activate in catalytic salt	2. Solubilize tin	2. Reduce
3. Electroless Cu or Ni	3. Electroless Cu or Ni	3. Electroless Cu or Ni

There is a quantitative difference, however, between the above processes when used on polypropylene or ABS surfaces. In general, due to the fact that conditioning processes for polypropylene seem more severe than those for ABS (perhaps due in part to the usually higher temperatures employed), polypropylene surfaces absorb more catalytic metal than do ABS surfaces. Oftentimes, this can be noted visually rather easily through a brownish darkening of the surface. This can not only lead to excessive loss of catalytic metal, but can also effect the performance of the electroless solution. This condition is quite manageable when proper process controls are enforced. However, this indicates again the need for somewhat better process controls overall when plating polypropylene than when plating ABS.

Either electroless copper or nickel may be used. However, as is well known, copper can have a deleterious effect on polypropylene so that electroless copper should be used only when a suitable grade of polypropylene is being used.

ADHESION VALUES OF METALS TO POLYPROPYLENE

It has been generally noted throughout the industry that Jacquet (pull) test values obtained on plated polypropylene, all other factors being equal, are significantly higher than on ABS. Since adhesion values are primarily established by the mechanical and chemical effects which take place during conditioning, it then follows that somehow conditioning affects polypropylene in a quantitatively different way than it affects ABS.

As far as the properties of the plastics are concerned, the Jacquet (pull) test is a measure of the tensile strength and Young's modulus of the surface layer which engages in plastics yield during pull testing. The bulk properties of polypropylene and ABS with regard to these two parameters are not sufficiently different to account for the big differences noted in the Jacquet (pull) test values obtained. Thus, there is only one possible conclusion: the tensile strength and Young's modulus of polypropylene in the surface layer are much less degraded by conditioning than is the corresponding case with ABS. This conclusion is probably consistent with the earlier observation that since polypropylene is harder to oxidize than ABS, it is less affected chemically by conditioning. Hence, the surface layer of polypropylene shows less chemical degradation than in the case of ABS.

06

METHODS OF PLATING ON PLASTICS

W. H. Toller

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This paper is a review of the literature of the various methods of making the surface of plastics especially ABS electrically conductive in nature so that the plastics parts can be electroplated in the same manner as metallic parts.

(author)

METHODS OF METALLIZING PLASTICS

There are several methods of making plastics conductive. These are: hot metal dipping, metal spraying, metal impregnation, chemical silver, conductive lacquer, vacuum metallizing, and electroless deposition (nickel or copper).

A. Hot Metal Dipping

Hot metal dipping is done by coating the plastics with a low melting point solder flux and quickly dipping the part into a low melting point molten metal. Upon withdrawal, the part has a deposit of metal fused to the solder flux. Because of the temperature restrictions of most plastics, this method is not applicable to all materials and not suitable for producing high polished decorative finishes.

B. Metal Spraying

Metal spraying is a process where metals can be melted in a special spray gun and sprayed onto the plastics surface to form a metal skin. It can be readily visualized that this process presents a number of difficulties.

Since the surface is nodular, its application as an initial metallic coating on plastics prior to electroplating is not practical due to the coarse grained structure of the deposit which produces a rough, irregular surface and much physical polishing is necessary to produce a reasonable finish. The process is used for electroforming particularly after electroplating as a thick metallic section can be built up quickly by this means.

C. Metal Impregnation

Metal impregnation is a method of incorporating metal powders in the plastics to give a metallic sheen to the molded part. The appearance is rather lusterless and dull and appears much like a plastics part which has been painted with silver or gold. The introduction of metal particles into the plastics has the tendency to produce brittle molding.

This method has been used to produce a material which can be electroplated directly, but the results are not completely satisfactory due to the difficulty of obtaining an even dispersion and as the surface conductivity is very low, coarse, rough plated deposits are obtained.

Somewhat similar in principle is the method of coating the surface of a plastics with wolloidal graphite which when burnished, produces a surface which can be electroplated. This system has been used for many years in the production of phonograph records.

D. Chemical Silver

In the chemical silver process, it is necessary to precondition the plastics prior to electroplating. The preconditioning is done to remove surface contamination, to provide a surface to which the chemical reduction coating will adhere, either by physical keying or by molecular bonding and to provide a surface that can become "wettable".

The surface contamination can be removed by placing the articles in a stainless steel basket and processing them in a proprietary cleaner at 140°F. The articles are rinsed and dried and then placed in a rotating drum with dry pumice for 10 to 15 minutes. After the articles have been depolished for the correct period of time, they are emptied from the barrel into a tray or sieve.

The pumice is removed from the parts by shaking and the collected pumice can be reused several times until it loses its abrasive quality.

Before passing on to the next stage, the parts must be thoroughly rinsed to remove all traces of pumice from the surface. From depolishing onwards, the lack of contamination is of vital importance. Since the remaining operations are chemical in nature, it is essential that the surface of the parts remain wet.

The plastics articles are dipped into a sensitizing solution containing stannous chloride, acetic and hydrochloric acids for two to 10 minutes. While the chemical reaction of sensitizing is not fully understood, some say that it produces a slight molecular change in the surface of the plastics which attracts the silver ions during the reduction process.

There is no doubt that sensitizing is essential to the silvering process and should be given every attention in its application.

After thorough rinse the plastics articles are placed in a polyethylene jar which has been filled two-thirds full with distilled water at a temperature of 60°F. (not over 80°F.). To this jar is added Silver Solution A (ammoniacal silver nitrate) and Reducer Solution B (formaldehyde or glycol triethanolamine). The jar is slowly up-ended to mix the solution gently, and then the jar is placed on a horizontal roller mill for approximately 10 minutes. If the chemical deposition has been carried out correctly, the parts will be covered with a deposit which is light gray in color. The solution will also have become gray and muddy. If the articles and the solution are dark or almost black, insufficient reduction has taken place and the jar should be replaced on the mill for a little longer time. If the articles are milky white and powdery and the solution is also milky, either the parts have been left too long in the solution or the temperature has been too high. White powdery deposits are usable but will produce a rougher finish after electroplate. After a thorough rinse, the articles can be racked for electroplating.

E. Conductive Lacquers

The spraying of conductive lacquers is one of the earliest methods of rendering plastics materials donductive. These lacquers contain electrically conductive pigments such as graphite, copper, silver or bronze powder. The chief difficulty associated with the use of lacquer lies in the fact that the pigment concentration must be very high to obtain continuous conductance through the coating.

Conductivity is sometimes helped by using the so-called "two lacquer" process. In this, the lacquer coating is first applied and after a short period during which the lacquer is allowed to dry, the conductive pigment is then applied in a solvent. By this means, the conductive pigment is not insulated by the lacquer to a great extent.

F. Electroless Deposition

The electroless deposition on plastics consists of clean, rinse, etch or condition, rinse, sensitize, rinse, catalyst dip, rinse and electroless nickel.

The cleaning usually is done in a mild alkaline-type cleaner containing a substantial amount of chelating agent at temperature of 120° to 140°F. Acid-type cleaners are also used.

The etch or conditioning solutions are strong chromic acid type with inhibitors and accelerators and usually proprietary in nature. The operating temperature will vary from 130° to 150°F. and the time varies from three to 15 minutes.

The sensitizing solutions are commonly made up of stannous chloride. The stannous chloride is absorbed on the properly prepared surface and into the pores. This step also seems to reduce any absorbed hexavalent chromium.

The catalyst dip is solution of palladium chloride or other precious metal. The palladium is reduced onto the stannous chloride already on the surface. The metallic palladium becomes the catalyst for the deposition of nickel or copper from the electroless solutions. After the surface has a uniform electroless coating, the plastics part is ready for electroplating.

Alternate electroless deposition processing steps are as follows:

alkaline soak, rinse, hot rinse, chemical surface conditioner, rinse, post-conditioner, rinse, catalyst, rinse, accelerate (Pd^{++} to Pd^{0}) rinse, electroless nickel or copper.

The alkaline soak cleaner is employed to remove any oil films, shop dirt, fingerprints, etc., from the molded parts. Immersion five minutes at 150°F.

The chemical surface conditioner is of the chromic-sulfuric acid type. Immersion five minutes at 145° to 150°F. at Baume 47° to 48°.

The post-conditioner solution is used to remove the surplus chromium-containing conditioning solution. Immersion one minute at room temperature.

The catalyst solution is a proprietary bath which revolves around a colloidal type of catalyst. This bath contains a colloidal dispersion of pre-reduced palladium metal in hydrochloric acid. Immersion two minutes.

The post-catalyst is carried out to insure the presence of metallic palladium on the plastics surface, initiating rapid electroless deposition of metal. Immersion 30 seconds at 100° to 110°F.

The electroless nickel deposits a thin layer of nickel to make the part metallic so as to be able to electroplate the article. Immersion six to eight minutes at 80°F.

BIBLIOGRAPHY AND REFERENCES

1. Furness, R.W., "The Practice of Plating on Plastics", published by Robert Draper Ltd., Teddington, England, 1968.

2. Muller, G. and Baudrand, D. W., "Plating ABS Plastics", published by Robert Draper Ltd., Teddington, England, 1967.

3. Goldie, W., "Electroplated Plastics", Electroplating and Metal Finishing, The Metal Finishing Trade's Journal, Vol. 18, No. 12 and 19, No. 1, December 1965 and January 1966.

4. Narcus, H., "Plating on Plastics", Plating, August, 1968.

07

PART DESIGN PARAMETERS OF PLASTICS SUBSTRATES FOR PLATING

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INTRODUCTION

A majority of the initial plated plastics products was introduced simply by plating existing plastics parts without design modification. Also, parts designed in metals were retooled, with only minor design changes, for plastics and then plated. Production problems on some parts necessitated modifications which were possible and practical with existing plastics molds. However, this was not always true and some applications failed to materialize.

Recently, a far greater number of parts have been conceived, designed and successfully developed to the production stage as plated plastics. This changing trend strongly reflects the need for applying current design considerations for maximum performance and economics.

The application of sound design fundamentals is equally important to the successful plating of either metal or plastics substrates. This paper discusses the fundamentals of plastics design and of electroplating design applicable to plastics for plating. It also covers design elements specific only to plated plastics composites. When possible, design recommendations are generalized. More specific details characteristic of the individual plastics are noted.

(author, modified)

But why is part design so important to the molder, plater, and users of plated plastics? They simply cannot afford to pay the cost resulting from the use of poor design practices. Improper part design results in increased rejects, longer plating cycles for minimum thickness requirements, increased costs, solution contamination, special handling and poor performance.

Deep recesses often necessitate increased plating cycles or special handling with confirming anodes; excessive plate build-up on sharp external angles or edges can destroy the design concept, abrupt changes in plastics wall thicknesses result in stress concentration and poor performance. Let's abandon these negative thoughts and discuss the specific fundamentals of design for plated plastics.

WALL THICKNESS

The wall thickness of a plastics part is greatly dependent upon the proposed part configuration and the ability of the plastics to satisfy the functional properties of strength and rigidty. Other factors must also be considered. For example, even with adequate strength and rigidity, the plastics flow would be severely restricted with a .010 in. wall thickness. Conversely, sinks, voids, ripples, and other defects may result from excessively heavy wall thicknesses (i.e., in excess of .250 in.) unless very special molding techniques are applied.

Completely uniform wall thickness is ideal but is rarely practical. Since changes in wall thickness are usually unavoidable, such changes must be gradual and adapted with generous radii to facilitate plastics flow and uniform stress distribution. Reduction in wall thickness is preferably progressive with the direction of plastics flow. These practices minimize flow turbulence which is commonly associated with surface imperfections and/or lower adhesion. (See Figure 1)

With respect to plating, it would be logical to assume that the wall thickness should be as great as economically feasible to provide greater rigidity and strength, and for ABS, to provide optimum adhesion as illustrated in Figure 2.

Likewise, maximum wall thickness promotes resistance to distortion from rack contact pressures at the plating temperatures of 150-175°F. This is a most important detail for polyolefin design.

But maximum wall thickness is not usually required and more generally not recommended for plating. The field experience with plated ABS indicates satisfactory performance with wall thickness typical of unplated ABS parts. The majority of larger plated ABS production parts have average wall thicknesses in the range of .090 in. to .150 in. Small, bulky knobs reach far greater thicknesses and with proper design, function satisfactorily. Also, existing production parts function satisfactorily with wall thicknesses below the above range.

Some performance problems have been encountered with bulky parts having a very high mass to plated surface area. Lower thermal cyclic resistance results because of the high thermal expansion "swell" of the plastics bulk and the relatively low elongation of the electroplate. Classic examples of excessive mass to surface area are included in Figures 3 and 4.

The plated spherical part failed three cycles 160/0°F, but the two-piece plated, snap-fit counterpart passed the required three cycles of 180/-20°F.

Figure 4 illustrates two methods of improving the performance of parts having a high mass to surface area. One technique provides a more uniform wall by removing the plastics bulk and adding a contrasting black plastics insert. A second technique provides external serrations to allow plastics expansion without cracking the metal plate. Both techniques have proven effective.

CURVATURES

Convex surfaces are easier to plate uniformly than flat planes. Broad surface expanses should have a minimum .010 in. to .015 in. per in. crown to improve plate uniformity and to more effectively mask small surface imperfections. Bright electroplate can greatly magnify even small surface imperfections. Crowning appears to mask the imperfections because the eye is not capable of focusing on a wide expanse of the curvatures as it is capable of doing on a flat surface (Figure 5).

Concave recesses can be plated providing the depression is not too deep. Deep scoops, flat-bottom grooves, and V-shaped grooves should be redesigned to improve plate uniformity. Depth of recesses should be no greater than 50 per cent of the width. Inside and outside corners should be rounded or chamfered. The minimum angle defined by the chamfer should be 100° (Figure 6).

RADII AND FILLETS

Radii and fillets are added to the plastics part to minimize stress concentration and to facilitate removal of the parts from mold cavities. They also facilitate plastics flow with smooth changes in flow direction, reducing turbulence. The examples in Figure 7 illustrate the preferred smooth plastics flow compared to the abrupt stop-and-go turbulent flow.

The examples also illustrate the more uniform part and plate thickness resulting with the radiused part. While smaller radii are considered acceptable, preferred minimum radii of 1/16 in. for inside angles and 1/32 in. for external angles are suggested (Figure 8).

All edges should be rounded to a radius of 1/32 in. to reduce edge plate build-up which could destroy the original design concept.

RIBS AND BOSSES

Ribs are added to plastics moldings to impart added strength and rigidity without increased wall thickness, to prevent warpage, and can be used to facilitate plastics flow. If improperly designed ribs can result in undesirable surface imperfections, including heavy sink marks which are highly magnified by bright metal plate. The results of electroplated ribs with proper and improper design are compared in Figure 9.

Two small ribs are preferred rather than increasing ratio height to the adjacent wall thickness above 3:2.

Bosses are studs or pads added to plastics part for reinforcing holes, anchoring inserts, or locating purposes. They also serve as knockout areas to facilitate part removal from the mold. All bosses should face the same direction. Bosses should be located in corners when possible, and the height should be no more than twice the diameter. Bosses can be used in combination with ribs for increased rigidity and to facilitate plastics flow. Fillets at the junction of the boss and the wall are necessary to prevent stress concentration at this point. Ribs and bosses must have adequate draft angles to facilitate easy removal of the part from the mold. Both ribs and bosses offer excellent locating points for plating rack contact tips and may be added specifically for this purpose. Suggested uses of bosses are illustrated in Figure 10.

Bosses are usually hidden in plated parts, but the general rule of generous radii on corners, fillets at the base, and height to width ratios should be applied for best performance.

OPENINGS

Narrow, closely spaced holes or slots can be more uniformly and easily plated if the corners are generously radiused. Figure 11 lists the minimum recommended radii for indentations of various depths.

Slots and holes should be no deeper than 50 per cent of the width or diameter. Distances between should be two times the width or diameter (Figure 12).

Open holes are preferable for complete drainage and rinsing during plating. Blind holes trap solutions resulting in misplate on cross-contamination of plating baths. Avoid blind holes with diameters less than 7/32 in. and attempt to limit the hole depth to half diameter. Countersink threaded holes to minimize plate buildup on the peripheries.

LETTERING, ETC.

Symbols for identification can be molded into the plastics part by indentation or as raised letters, figures or other marks. A given letter or figure should be elevated no more than half the width; however, a height of .010 in. is commonly accepted for adequate detail. All edges should be rounded with a preferred minimum radius of 1/32 in.

Indented symbols are often molded into the plastics part and after plating, are filled with a wipe-in colored paint for a pleasant contrast with the metal plate.

DRAFT ANGLES AND UNDERCUTS

Draft angles are added in combination with radii and curvatures to facilitate part removal from the mold. Draft is added to both internal and external wall surfaces. Minimum draft of one degree is recommended; however, larger draft angles may be desirable since mold release agents are not used during molding parts for plating.

Undercuts have been satisfactorily adapted for plated plastics parts to allow snap fits for subsequent assemblies. For plated plastics, undercuts are less easily designed because allowances must be made for the electroplated metal thickness. It is quite important that removal from the mold not tear the undercut material surface since adhesion and appearance could be affected.

SHRINKAGE

Shrinkage is most important to proper mold design, but must also be considered in part design. For example, uniformity of part wall thickness is more critical to assure proper fill, pressure, and cure with plastics having high shrinkage properties. Likewise, very heavy sections are undesirable for such plastics materials.

SPECIAL EFFECTS

Textured patterns and matte finishes are useful tools to enhance part appearance and to cover minor molding or plating imperfections. The desired textured patterns are produced in the mold surface and imparted to the molded plastics surface. Uniform matte finishes are best achieved with peating solutions developed specifically for that purpose.

MISCELLANEOUS

Concave recesses may create wells to trap and hold plating solutions. When such design is necessary, small drainage holes should be added to alleviate this undesirable condition.

As previously mentioned, openings and protrusions can be used to locate plating rack contact tips for mounting the parts. Rack contact can be made to hold parts in tension or compression. Preferably, rack contact should be located in non-appearance areas. Double contact is suitable for knobs and small escutheons; however, multiple contact areas are required to provide the proper support and adequate current for plating larger parts. Four corner contacts may prove adequate for parts up to 6 in. x 12 in. while larger parts commonly require additional points of contact. Parts are normally racked with the longest axis in a vertical position to minimize the inclusion of any solids (shelf roughness) on horizontal planes.

Conforming anodes can be used to more uniformly plate internal surfaces, i.e., coffee pots and other low-current density areas. The designer must be aware that such anodes are quite expensive and the techniques more involved and time consuming than standard plating practices. The net result is added expense.

When possible, mold parting lines and gates should be located in non-appearance areas. Gates should be located in the heavier wall areas to facilitate unrestricted plastics flow into the part.

SUMMARY

For maximum resistance to extreme temperature changes and to corrosive environment, uniform thickness is desirable in both the plastics substrate and the electroplated metal composite. Gently curved, convex surfaces, radiused angles, and minimum protuberances promote more uniform thickness and minimum stress concentration. These are some fundamentals of good plated plastics design.

We have endeavored to cover the more important fundamentals of design applicable to plastics parts for electroplating. This work will never be complete since each new material, process, or technique will obsolete some present ideas, and reveal the need for new and improved design information. It is believed that this paper will serve as basis for compiling new information and field experiences by the Technical Committees of the Society of Plastics Engineers, American Electroplaters Society, American Society of Electroplated Plastics, Inc., and American Society for Testing and Materials. Finally, to reiterate the primary thought, you simply cannot afford to pay the costs resulting from the use of poor design.

BIBLIOGRAPHY

1. Design and Converting Techniques for Plating Cycolac Brand ABS EP-3510, Marbon Div., Borg-Warner Corp., Tech. Bull., May 1967.

BIBLIOGRAPHY (Cont'd.)

2. Versaw, W.D., "Keys to the Profitable Production of Plated Plastics Parts", Soc. of Plastics Engineers Technical Papers Vol. XIV.

3. "Design of Molded Articles", Plastics Engineering Handbook of the Society of the Plastics Industry, Inc., Third Edition, Rheinhold Publishing Corp., New York, N.Y., 1960.

4. "Part Design", Celcon Acetal Copolymer Design Manual, Chapter 3, Celanese Corp. Tech. Publ.

5. "Design Details", Designing Matched-Die Molded Fiberglass Reinforced Plastic Parts, Owens-Corning Fiberglas Corp. Tech. Bull., Feb. 1963.

6. "How to Design for Better Platability", Products Finishing Reprint from September 1962.

7. Safranek, W. H., "The Role of Design in Better Electroplating", Metal Progress, June 1968.

8. "Injection Molding with Polypropylene Homopolymers and Copolymers, Rexall Chemical Company Tech. Publ.

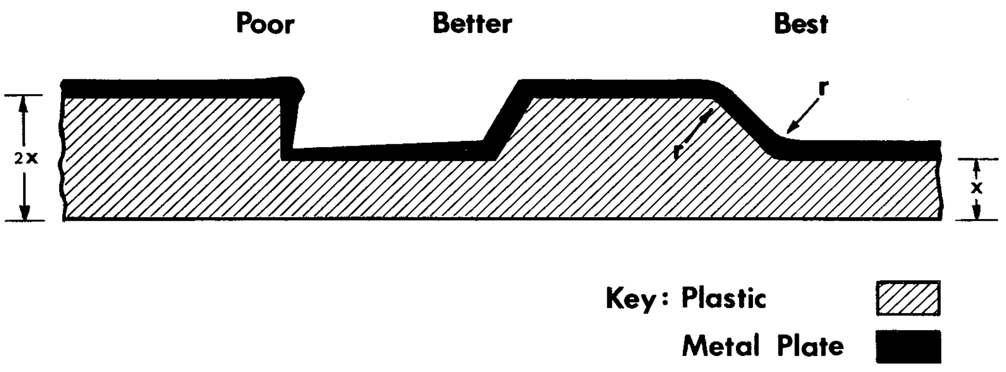


FIGURE 1

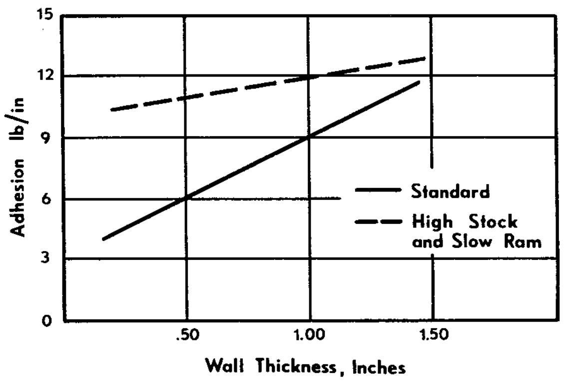
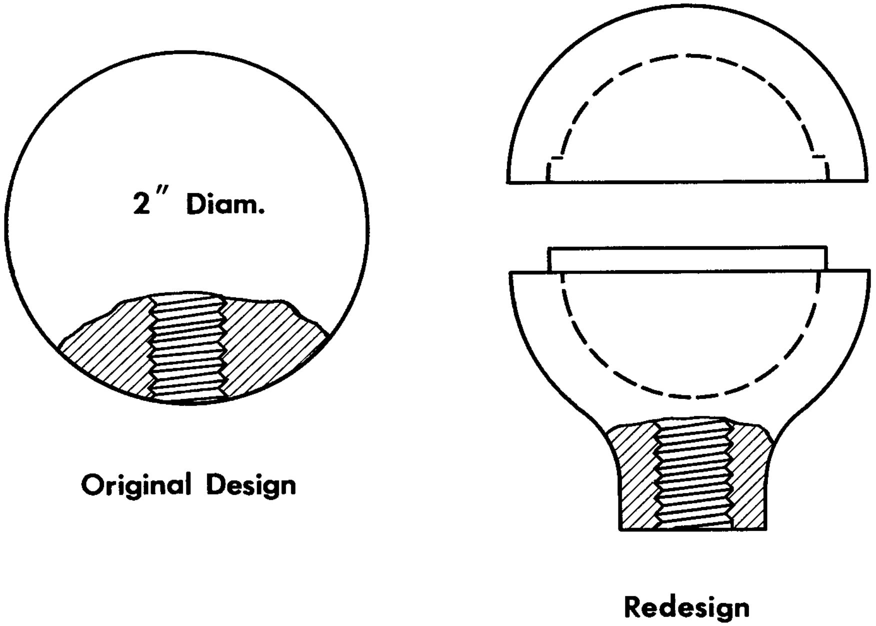


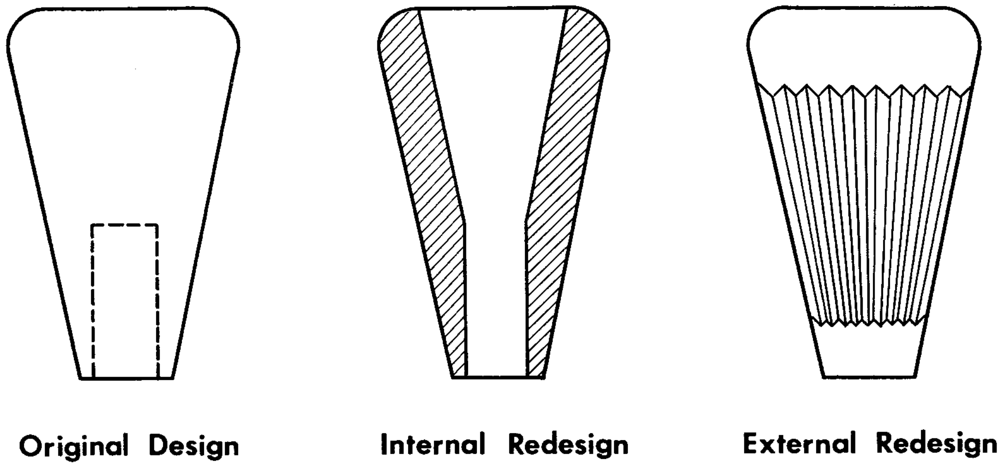
FIGURE 2



Original Design

Redesign

FIGURE 3



Original Design

Internal Redesign

External Redesign

FIGURE 4

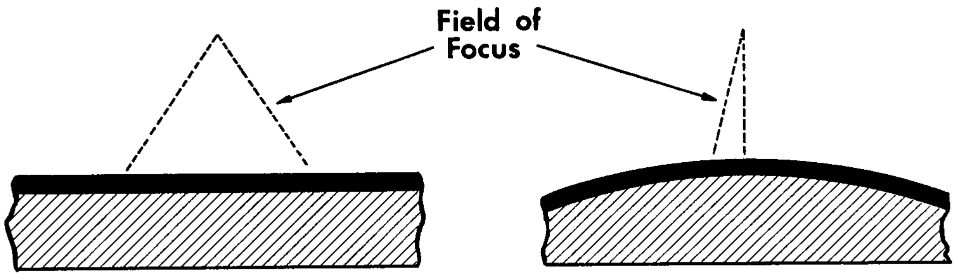
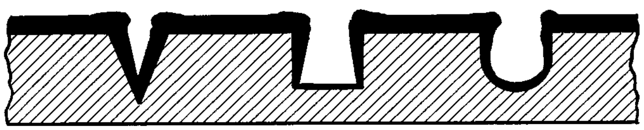
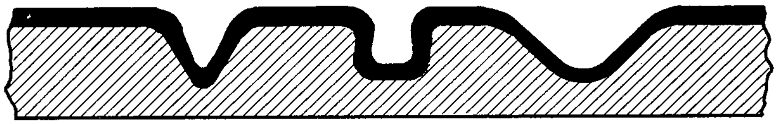


FIGURE 5

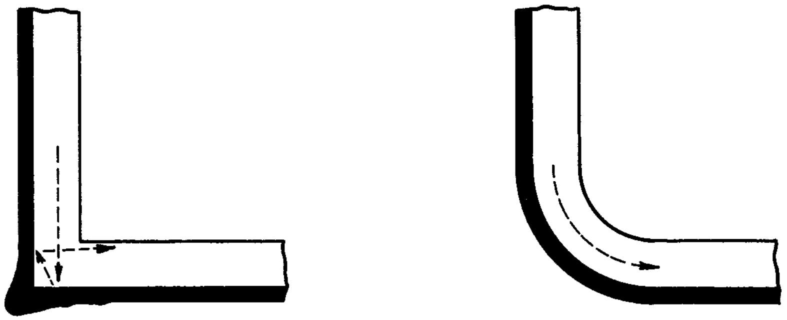


Poor Design



Improved Design

FIGURE 6



Turbulent Flow

Smooth Flow

FIGURE 7

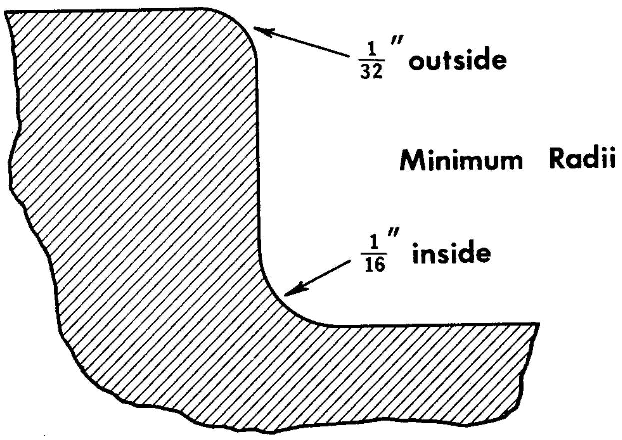
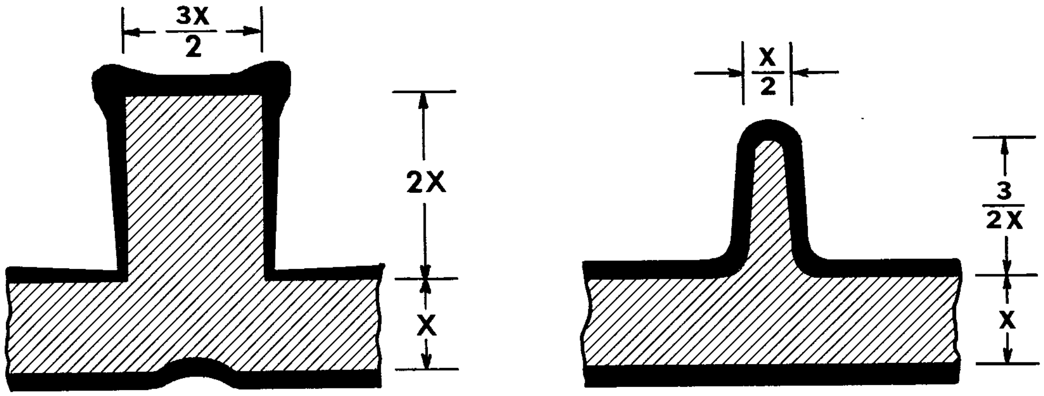


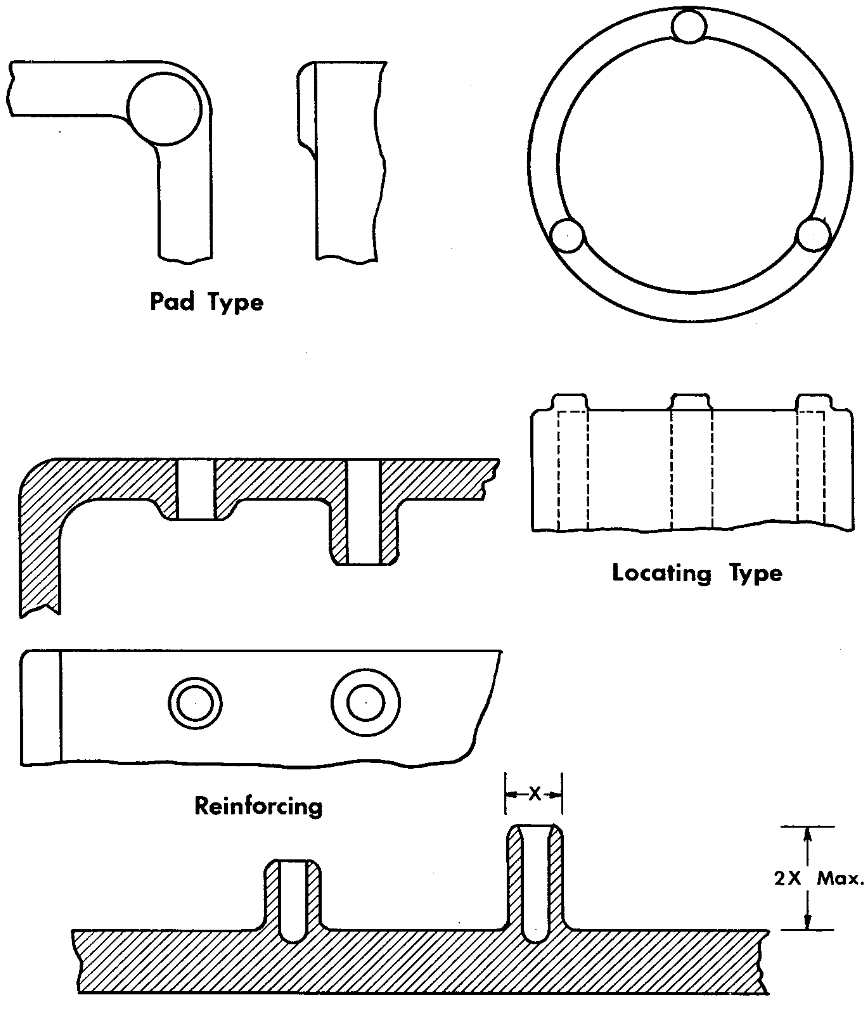
FIGURE 8



Improper

Proper

FIGURE 9



Pad Type

Locating Type

Reinforcing

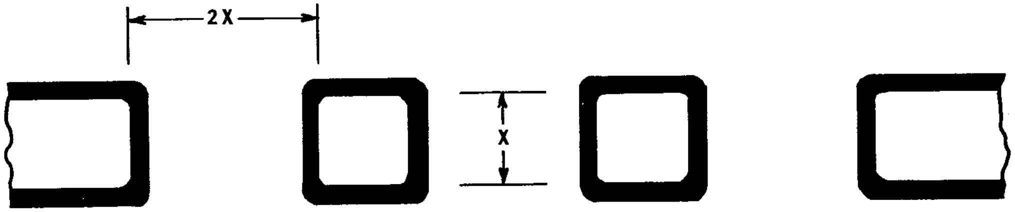
Screw Holding

FIGURE 10

Depth of Indentation	Minimum Radii For Corners
1/16 inch	1/64 inch
1/8	1/32
1/4	1/16
3/8	3/32
1/2	1/8
1.0	1/4
1.5	3/8

FIGURE 11

Improper Design



Proper Design

FIGURE 12

08

METAL PLATING SYSTEMS FOR ABS AND POLYPROPYLENE

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and

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The market for plated plastics has grown over ten-fold in the past three years, from 1/2 million pounds in 1964 to 6 million pounds in 1967.[1] ABS has been the principal plastics used for plating, and to date, most of the applications have been small parts for interior or relatively non-corrosive environments.[2] The plating system for interior applications is relatively simple, consisting of 0.5 to 1.0 mils of bright acid copper, 0.2 to 0.3 mils of bright nickel and 0.01 mil chromium. This system is by far the most popular and widely used finish for interior parts for the following reasons:

1. Copper plated from bright acid baths is more ductile and has a higher coefficient of expansion than either bright or semi-bright nickel. These two properties are helpful in accommodating the higher coefficient of expansion of ABS.

2. Bright acid copper is less expensive than bright nickel and has excellent leveling that helps to hide small surface defects. Less bright nickel is needed then to achieve a bright smooth surface for chromium plating.

3. Thin bright nickel, 0.2-0.3 mil, and 0.01 mil chromium is sufficient to provide some corrosion protection in mild environments and also allows for good color matching with other plated parts.

It is also worth mentioning that while bright chromium is the most popular decorative finish, other finishes such as brass, bronze, silver, gold, tin, could easily be applied in place of chromium.

However, while interior parts will probably constitute an ever growing market for plated ABS, a much larger market for exterior parts exists and is as yet largely untapped.[2] Based on projected estimates of 30 to 40 million pounds by 1970 for plated ABS, it is apparent that these forecasts must include such large volume markets as exterior automotive and marine parts. The automotive market alone could consume 50 million pounds of plated plastics for such items as grills, wheel discs, front and rear light bezels. Already some automotive exterior parts are being tried on a limited production basis and many more are being considered.

What sort of plating systems are needed for exterior parts? It has been our experience that the plating on plastics must be equivalent to what is now being used to protect zinc die castings. It is most important that corrosion does not penetrate the plating and reach the plastics interface. If this occurs, then the corrosion spreads laterally at the interface and large blisters form under the plating.

In order to study the effect of accelerated corrosion on the durability of plated plastics, polypropylene was used as the substrate.This was done to avoid as much as possible the formation of any blisters due to low adhesion or thermal cycling failures. In general, minimum peel strengths of plated polypropylene used in our tests were in excess of 15 lbs./in. and no failures occurred due to thermal cycling alone. Results of combined thermal cycle-CASS testing are given in Table I for five plating systems and compared to steel panels similarly plated. The numbers given in Table I are either blister count on the polypropylene or rust spots in the case of steel. The data can be interpreted as follows:

System 1

The plating on polypropylene is penetrated in less than 16 hours, which is unusually rapid. More blisters appear after 32 hours and a large number after 48 hours. This is typical performance for a semi-bright, bright nickel system but the number of failure sites is much greater than observed on steel substrates. Correlation with one year's roof exposure is good.

System 2

Doubling the semi-bright nickel thickness gives much better corrosion performance on steel, requiring over 32 hours of CASS exposure for penetration. However, little improvement occurs in the case of polypropylene since the coating is still penetrated in less than 16 hours. This suggests some influence of the substrate on the quality of the plating. The fewer blisters that appear after the third cycle compared to System 1 are attributed to the thicker semi-bright nickel layer.

System 3

Addition of 0.1 mil of bright nickel containing finely dispersed inorganic particles (denoted as Dur-Ni^R Nickel in Table 1) on top of bright nickel creates micro porosity in the chromium layer. This acts to spread the corrosion out over a larger area and reduces the amount of penetration at individual corrosion sites. A definite improvement is seen on plated steel compared to System 1, but only a slight improvement on plated polypropylene. Blisters appear on the second rather than the first cycle and their total number is slightly less after the third cycle. Again, an influence of the substrate on the plating is indicated. Roof exposure and CASS show fair agreement.

System 4

This system should be compared to System 1 because the nickel thicknesses and ratios are the same, and also to System 2 because the total plate thickness is the same. It can be seen that the corrosion performance in CASS of both plated steel and polypropylene is improved when 0.5 mils bright copper is used with duplex nickel. However, industrial roof exposure was poor and contrary to CASS. Without microporous chromium, copper does not improve duplex nickel performance on exterior exposure.

System 5

Excellent corrosion performance is seen when both acid copper and microporous chromium were used together with semi-bright nickel. Correlation is good between CASS and roof exposure.

Additional studies established the following points:

1. No failures occurred due to thermal cycling alone. If CASS testing was carried out for 48 hours and then the panels were given one thermal cycle, the number of blisters was essentially the same as those given in Table I. This shows that corrosion is necessary to produce the blisters.

2. Thermal cycle-CASS results of plated ABS using Systems 1, 3, 4 and 5 were very similar to those obtained with plated polypropylene.

3. Cross-sections of blisters on plated ABS or polypropylene showed either no electroless nickel or an electroless nickel layer too thin to be resolved by the light microscope in the area of the blister. Some electroless nickel could be seen in areas of the cross-section adjacent to blisters where adhesion of metal to plastics was still good.

These findings indicate that (1) the electroless nickel was dissolved by corrosion of the CASS electrolyte or (2) no electroless nickel or a very thin electroless nickel was present at the start. The very large size of the blisters and the observation that they occurred so rapidly seems to argue against the first possibility. Thus, some consideration was given to finding a method which would show whether or not thin or bare spots were present in the initial electroless nickel layer.

After some experimentation, it was found that masking with platers tape one side of an unfilled translucent ABS or polypropylene panel before preplating, then removing the tape, and inspecting the electroless nickel in a darkened room with a high intensity light source, numerous holes or skips could be seen in the electroless layer. As many as 20 to 30 holes were detected on a three by four in. panel. Approximately 25 per cent of these persisted after a 0.5 mil semi-bright nickel or acid copper were applied. A few holes were sometimes visible at 1.0 to 1.5 mils total plate thickness.

The incidence of corrosion sites forming at places where holes exist in the electroless nickel is high. By marking the location of the holes in the electroless nickel and then plating to the thickness used in Systems 1 or 4 of Table I it was noted that blisters formed in these areas after CASS testing. Correlations in most cases were better than 50 per cent and as high as 85 per cent. Thus, the existence of holes in the initial electroless nickel layer and their correlation to corrosion blister sites can explain the more rapid failure of Systems 1, 2 and 3 of Table I. However, the better corrosion performance of Systems 4 and 5 is not fully understood and cannot be explained at the present time.

Various methods have been tried to eliminate the holes or skips in the electroless nickel film. Fresh solutions, different compositions, wetting agents, temperature and time variations, and agitation were all unsuccessful in eliminating or modifying the problem. From our work to date, it appears the skips form at the activation or nucleation stage by non-uniform adsorption of the palladium catalyst. Whether this is the real cause or whether it originates in the plastics surface has not been determined. This is a problem which is going to require a great deal more study before it can be resolved. But a successful solution holds the promise of much better adhesion, thermal cycling, and corrosion performance for plated plastics.

In conclusion, the following plating system has been found to perform quite well on exterior parts that were properly molded and preplated:

0.8 mil	bright acid copper,
0.5 mil	semi-bright nickel,
0.3 mil	bright nickel,
0.1 mil	DurNi$^{(R)}$ Nickel,
0.01 mil	chromium.

Both ABS and polypropylene parts have passed three combined thermal cycle-CASS tests for a total CASS exposure of 48 hours. Pending new test results from the ASEP corrosion program now on exterior exposure, the above plating system represents the best combination that we know of to meet both thermal cycle and corrosion requirements of plated plastics.

REFERENCES

1. Products Finishing, May 1967.

2. Hepfer, I.C., et al, Plating, 1968.

TABLE I

THERMAL CYCLE - CASS TESTING OF PLATED POLYPROPYLENE

	Plate Thickness* mils					Number of Blisters or Rust Spots						
						Cycle 1		Cycle 2		Cycle 3		
System No.	Acid Cu	Semi-Bright Ni	Bright Ni	Dur-Ni$^{(R)}$ Ni	Sub-strate	TC	CASS 16 hrs.	TC	CASS 32 hrs.	TC	CASS 48 hrs.	Ind. Roof 1 yr.
1	0	0.5	0.3	0	PP Steel	OK	1 - 11 0	-	5 - 15 2 - 10	15-30	7 -100 7 - 50	76-128
2	0	1.0	0.3	0	PP Steel	OK	1 - 9 0	2-20	- 0	-	2 - 20 0 - 10	Not Tested
3	0	0.5	0.3	0.1	PP Steel	OK	- 0	-	40 - 80 0	-	40 - 80 1	25-36
4	0.5	0.5	0.3	0	PP Steel	OK	- 0	-	Dark Spots 0	-	2 1	100
5	0.5	0.5	0.3	0.1	PP Steel	OK	- 0	-	- 0	-	OK 0	*

PP - Polypropylene

*All samples have 0.01 mil chromium as top layer.

09

MEANINGFUL STANDARDS FOR PLATED PLASTICS

A SUMMARY OF ASEP AND ASTM PROGRESS

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Since the fall of 1965, several groups in ASTM, and for a lesser time, in the American Society for Electroplated Plastics, have been struggling with the establishment of industry standards for our complex field of electro-plated plastics. Viewpoints of platers and molders, as well as users, vary in as many or more directions concerning the operations surrounding the processes as there are people working to establish the guidelines for the industry. I will try to enumerate the major steps that have been taken to establish basic thinking and action.

The most difficult thing to overcome in setting these guidelines is the complex nature of the overall process of molding and plating as it is related to the myriad base materials and applications. Where one test may prove advantageous in the establishment of procedures for one material, it may have no application whatsoever for a different material. Introduce, then, into this pattern several basically different materials, as many conflicting molding conditions as there are molders, advantages and disadvantages of molding equipment, local weather conditions affecting molding operations, and the degree of excellence with which the plating process is controlled, mix this well with the desires, ambitions, aspirations, and expectations of your customers, and you have a universally unpalatable recipe, or a pattern of such confusion there is not an artist or engineer brave enough to put his name to the creation.

To accomplish the setting of these standards and their validating tests, men were recruited from every facet of the industry. Both ASTM and ASEP now have representation from molders, platers, molder-platers, end users, resin producers, and suppliers of molding and plating equipment and chemicals. Within these have been formed industry groups, whose sole purpose is to establish communication with industries having similar performance requirements. These four areas are:

1. automotive, marine,
2. plumbing and building,
3. major appliance (including radio, TV and small appliances), and
4. miscellaneous tool, hardware, mechanical and electrical manufacturers.

Their communication is specifically the purpose of liaison, concerning the standards suggested, and developing acceptance at the user level.

Other committees in both organizations have been formed with specific goals, such as: development of a standard test panel, establishment of adhesion tests and procedures, corrosion tests, visual inspection, design data, and a final group for writing the tentative specifications.

Before any specification, standard, procedure, or test can be suggested, there must not only be a method of testing, but something upon which to run the tests, which will be common to all participants. As a result of long study involving all of the facets of industry standards considering plating, molding, area, surface and configuration, it was decided a plaque three in. by four in. by 1/8 in., flat on one side, but with a convex curvature on the other side, approximately .015 in./in., giving a crown of .020 in., would more nearly duplicate the majority of configuration problems encountered than any other standard shape possible.

The evaluation of various problems in the field produced three major areas where concentration of the effort was indicated; thus, the initial attention of both ASTM and ASEP was drawn to adhesion, appearance, and corrosion resistance. The first two have the most widespread interest, while the third, probably more important from the viewpoint of plating volume, is of interest in exterior applications. Adhesion had been, and still is, checked, for the most part, by performing a peel test. There has been some dissent in the use of a flat part for such tests, the claim being based upon the fact that a peel test on a flat is not really a true peel, but a torque test, because the pull cannot be exerted in a straight upward motion. The dissenters suggested a cylinder be used for such tests where it could be properly mounted, and the pull made in a truly upward motion with the cylinder turning. The problem with this method is the introduction of a configuration not common to the majority of production parts. Additionally, the plating of such a cylinder is accomplished by rotating the part in the electro baths to insure proper and equal coverage over the entire diameter. Since neither this process is common to the industry nor the shape common to normal present design, it has been decided to stay with the plaque.

Poor adhesion can be the result of molding deficiencies, improper plating procedures, or solution control. For ABS materials, molding can be checked readily with the glacial acetic acid test. In ASTM and ASEP, tests have been conducted in a variety of plants using several methods. All have been of the glacial acetic acid type having minor variations, and one is now ready for joint membership balloting prior to public announcement. This test, although not totally infallible in ABS, has no bearing on other materials such as polypropylene, plexiglass, PPO, phenolic, or epoxy. Although each of these latter materials evidence, in my personal experience, greater adhesion than ABS, there are problems from time to time, and tests will have to be established by the committee assigned to this work.

The committee on design has a major role in the area of adhesion, since gating plays such an important part in the production of parts for plating. It is their job not only to recommend proper gating procedures as to size and location, but general design standards covering runners, radii, wall thickness, grooves, recesses, bosses, ribs, mold surface finish, inserts, rack contact areas, and dimensional allowance for plating build-up. Much of their work, although not yet officially published by the governing organizations, is being followed and the results carefully studied. It is expected they will publish tentative standards covering design for member balloting in the near future.

Closely related to the adhesion specification is the thermal cycling of plated parts. This test, probably more than any other, has been most difficult to cope with. Many processors cannot understand the reason for the test, especially in cases where great temperature change is not apt to be present in the final application. There are, however, drastic temperature changes when shipping parts, especially during the cold winter months, when extremes of cold and heat could cause abnormal expansion and contraction, resulting in cracks and general deterioration of the parts. So complex has this specification become that the committee with this responsibility has recommended three separate tests dependent upon the end use of the parts.

Normal use	0° to 150°
Low temperature	-30° to 120°
High temperature	30° to 180°

Platers and end users have been requested to test some of their work at the above temperature ranges to determine how the parts responded to the cycling, and how many cycles are necessary to cause failure. A total cycle time of one hour has been suggested. The results of these tests have been correlated with failures in the field through the industry group, and the information is being compared so that realistic thermal cycle temperature ranges can be achieved.

There exists one great problem in the use of these thermal cycle tests in the time required to make them. In our high-production shops, the number of parts produced in one hour could be a major problem to the processor. If, in that hour, he produced several thousand parts, they could all be defective before he knew of a problem. Nor is the test infallible. In one case, parts that failed thermal cycle gave no problem whatsoever in the field. The parts were shipped during the winter, remained in transit for five days, and upon arrival were found in perfect condition. Conversely, a group of parts that did pass thermal cycle at the time of production, failed a similar test several days later in the producers plant. Thus, thermal cycling remains questionable in its present form.

The committees handling this specification have left nothing to conjecture, performing static hot and cold tests, thermal cycling tests using cold air to hot water and hot water to cold air, refrigeration to ovens, and in a further attempt to reduce the test time, are correlating the result of thermal shock tests with field results.

One of the more important areas to be covered is that of visual acceptance, which accounts for the majority of rejects. Since this cannot be an actual specification, proven one way or the other by definite tests, and is, for the most part, a matter of opinion, it was decided to approach this phase from the viewpoint of setting a quality control level as opposed to a standard. A large group of users was canvassed with the outline of this proposal, and from them has evolved an inspection guide table covering 16 possible defects and acceptance or rejection areas based upon their location, number involved on the part, and their proximity to each other. In addition, as a part of this guide, definitions of molding terms and plating terms have been included to simplify and clarify the intent of the guide. This phase of the work is complete to the point of balloting membership for opinion in both ASTM and ASEP.

The introduction of new materials to the plating field and their inclusion in exterior applications has necessitated an accelerated program for corrosion testing and establishment of standards in that field. Salt spray is again being examined, not only for type, but length of test, to determine compatibility of the process in applications so exposed. Corrode KOTE and CASS tests are being run with varying effect on plated parts by several processors and users with the results being correlated, where possible, with field data. In this case, it is not only the length of the test, but the configuration of the part being tested and the amount of metal deposited, that contribute to the complexity of the problem. Another factor to be considered in this program is the SAE dust test for automotive applications and these are being conducted now with results expected before the end of the year.

In addition to these tests, the corrosion committee is conducting research into the effect of humidity as it is related to temperature upon plated plastics and aerated water for its effect in promoting degradation of the surface. Special tests for resistance to perspiration, skin acids, fruit acids, alkalies, and detergents are under way, specifically for the appliance industry. This work is long and tedious, requiring the total cooperation of every member of the organizations involved, whether they be processor or user. It requires extensive laboratory facilities, time and patience, and all these have been offered without restraint of any kind.

Determining what should be done is a major job in itself. A few people could sit at a table and enumerate what, in their opinion, were the points that should be covered, but that in itself would be totally incompatible with the industries involved. In order to prevent this, a committee has been formed to collect and compile from industry exactly what their requirements are. They cover every possible avenue from automotive to curtain rods. Theirs is the job of bringing data to the various standards committees from industry, indicating where they have had problems, where they feel improvement could be made, and what they feel will be required in the future. This data is compiled into categories that correspond, as closely as possible, with the committee structure of ASTM and ASEP and given to them for inclusion in their programs. Such work sounds very simple, but it is far from that. It means close contact with literally hundreds of people and the compiling of all the data received. It is a job that must be done, and is being done.

Much in the same category is the group who collect and report field service data. Theirs is not only an interest in the failures, from which we can evolve remedies, but the successes from which we can evolve positive action regarding specific situations and applications. Information of this type is as valuable in the establishment of standards as the validating tests themselves, and is necessary to the continued progress of our industry.

Compiling of industry requirements, field service data, and perfecting of tests, are all preliminary to the final and most demanding work in establishing industry standards. Standards for any procedure, process, or function, must be so written that they are absolutely clear in their intent, and positive in their direction. Anything less than this contributes, in great measure, to confusion, misunderstanding and eventual failure of the project to be accomplished. Very simply stated, standards are a set of specifications supported by validating tests, acceptable to all those involved in their use. They must be written so that interpretation is not necessary, nor adherence to their parameters will exert undue pressures upon the users. Thus, the final act of establishing industry standards falls to the committee assigned to write the specifications and spell out the tests. These committees have been formed in both organizations, and have already started their work for membership balloting.

Since the fall of 1965, much has been accomplished. In ASTM, committee B-8 has reactivated their plating on plastics group. Committee D-20, dealing with substrates, has activated a group to deal specifically with plastics materials for plating.

ASEP was formed to bring together molders, platers, suppliers and users whose only interest is the plating of plastics. The two organizations have joined their efforts to more rapidly come to the conclusions we so sorely need, and to prevent, as much as possible, overlapping of work. There are now ready for balloting in these organizations, specifications for a test panel, an acetic acid test and precise instructions for its use, a visual inspection guide for quality control and design specification, and a standard design guide for electroplated plastics. In process and under examination, but nearing completion, are the standards for thermal cycling and corrosion testing.

Much has been done. Much more remains to be done. New materials, new applications, new processes will demand review, refinement and rewriting of the standards we set today. It can only be accomplished with complete cooperation and participation of all involved - the molders, the platers and the users. <u>You</u> are the industry. These are <u>your</u> standards. They require <u>your</u> attention.

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FUTURE OF PLATED PLASTICS IN APPLIANCES

Don M. Courtad

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Major Appliance Divisions

Much work has been done in the application of plated plastics parts to appliances, and much experience and knowledge has been gained in the process. All of the experience thus gained does not, unfortunately, fall under the category of good experience.

However, as I pause here at this point in time, and think about our attempts to use plated plastics, some successful, some not, I feel safe in saying that we in the appliance industry have an acceptable understanding of the technology involved to successfully design and use plated ABS parts. I only wish that we understood the use of plated polysulfone, polypropylene and phenolic as well.

The knowledge required to utilize these materials undoubtedly is, or will be, available and we can now consider the future uses of the broad spectrum of electroplated plastics parts.

Historically, perhaps the largest single use of electroplated plastics in so-called "Consumer Products" has been knobs. I ebelieve we will see the platable plastics with temperature resistance inherently higher than ABS invade the knob applications of ranges, portable heating appliances, etc. In addition, end caps for control panels, and even control panels themselves on these higher temperature appliances are being evaluated.

In the area of portable appliances, entire housings have been made from ABS and undoubtedly plastics with resistance to higher temperatures will open broad new avenues of design.

To my knowledge, no plated plastics part has been used in an appliance for purely functional (i.e., in a location not seen by the consumer) use. The ability to encapsulate a plastics part in a hard, wear and abrasion resistant case should, and undoubtedly will, initiate some thinking along functional lines.

In summary, I am sure that as the design and economic considerations are worked out, and new processing techniques developed, many new and novel decorative, as well as functional, applications will appear in the appliance industry.

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THE FUTURE OF PLATED PLASTICS IN PLUMBING

L. K. Jones

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Ten years ago most plumbing manufacturers would have stated that the future of plated plastics in plumbing products was pretty doubtful. The reason for this was that plating of plastics at that time was restricted to the vacuum plating process and durability of these finished parts was far below acceptable standards for either brass or die-cast zamac components.

Our company and others in the plumbing industry had developed certain unplated plastics components successfully as substitutes for metals and it was our feeling that, if a satisfactory plating process could be developed, a whole new field could be opened for plastics in plumbing.

In 1964, we instituted a research program in conjunction with the Physics Department at West Virginia University to develop a plating process that would provide an acceptable finished product that could be used as a substitute for metal. Our program was based on the development of an electron bond between the plastics base and the plating materials rather than an encapsulation process which had been developed by certain plastics and plating equipment producers. Our eforst were encouraging if not rewarding. We found that by irradiating certain materials that we could produce a bond much more durable than vacuum plating or encapsulation. The chief drawback in the process was a change in the mechanical properties of the material to be plated which rendered it all but unusable in most applications.

The second approach which we took was toward a chemical treatment which would inhibit the surface and structure of the material to be plated with free electrons of a platable metallic salt that could then be electroplated. During the second year of this program, one of the major producers of plastics introduced a process whereby certain ABS plastics could be plated electrolytically. We investigated this process and found it to be suitable for certain plumbing product applications.

Within the next two years our company increased the usage of plated plastics from zero to 132,000 pounds per year. Having had some considerable experience in the use of plastics in plumbing products we restricted our design and usage to decorative components. Our initial products were items such as shower head covers, stream formers for sink and lavatory faucets and other non-mechanical parts. Experiments with functional mechanical components led us to believe that through proper design the use of plated plastics components could be expanded substantially.

In 1962, we introduced a redesigned single control faucet line that incorporated certain plastics components. We found that these components could be plated and would function equally with their unplated counterparts. There was, however, a reluctance on the part of plumbing contractors to accept these substitutes. We had in design process at this time an entirely new faucet concept which we ultimately decided to introduce with certain chrome plated plastics components. Our experience with these parts was most encouraging and from it came the numerous parts which we produce and market today as a part of our plumbing products line.

All of this brings us up to date insofar as plated plastics in plumbing are concerned. What of the future of these materials, which is the topic of our presentation and of significant interest to all present?

We estimate that the potential in pounds of plating grade plastics, as we now know them, could run as high as 10 million pounds per year within the next five years. The only limitations imposed on this usage is the acceptance by the industry of these materials and the care of designers and manufacturers not to exceed the physical capabilities of these materials. Time and change are on our side in this endeavor.

The demand for plumbing products is increasing each day in our expanding population. By 1971, over 50 per cent of our population will be in the age group under 25 years. This generation of new homemakers have had more and better experience with plastics materials and as a result are more receptive to products made from them. Economics will also play an important role in this change. The cost of producing and finishing the traditional plumbing materials has increased at an exdessive rate in comparison with other materials used in consumer products. In order to retain and expand their position in the struggle for consumer dollars, producers of plumbing products must develop a more imaginative attitude toward the design of their products, the materials selected and their ultimate use.

It has been said that "haste makes waste" and in the case of plastics this has been a most unfortunate fact. Producers of plastics materials have pushed products on to the market without sufficient testing to provide designers and users with adequate data to properly evaluate them. Excessive zeal to recover research and development costs have ended in near disaster for many well-conceived products and unwarranted criticism for those who marketed them. Our company has shared in some of this misfortune so I speak with authority on this subject.

We are a nation of "doers", however, and the consumer is fortunately forgiving.

Let us take a look at the future of plated plastics and some of their possible applications in plumbing.

Those of you who visited the rest room of this fine establishment probably did not take particular notice of the flush valve on the water closets and urinals. This particular product has a very difficult shape to finish, not by necessity but rather by design. Suppose we were to make the parts from theconventional materials but encase them in a modern, attractive shape made of chrome plated plastics. The finishing costs of the present shape would more than pay for the added parts and an easier to clean, more sanitary product would result. There were 20 million of these valves sold last year - an interesting challenge.

Each morning when you brush your teeth you use a lavatory faucet in your bathroom. Here again is a difficult to finish shape by nature of its design. It has already been replaced by a chrome-plated plastics cover by at least one leading manufacturer and will be replaced by more in time. Potential? There will be over one and one-half million homes built this year and each one has from two to three baths. Add this many more to the replacement market and you have six million faucets with exposed parts of chrome-plated plastics.

This evening your wife went to the kitchen sink to rinse off the dishes before placing them in the dishwasher. In doing so, she used another plumbing item, the kitchen sink faucet with its swinging spout to reach both bowls. Numerous attempts have been made to glamorize this product with varying degrees of success. The plumbing industry consumes some four to six million of these faucets each year.

Gentlemen, the field is open to chrome-plated plastics in plumbing. The only boundaries are the imaginations of those who develop the processes for better materials and finishes and those who design the products.

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PLATING ON PLASTICS - A PRAGMATIC LOOK AT THE PROBLEMS

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ABSTRACT

In spite of progress being made in the plating of plastics for automotive applications, a number of critical problems still remain unsolved. Some methods are suggested for extracting the maximum amount of information from the test programs being carried out by both suppliers and users. Specific items to be discussed will include adhesion testing, thermal cycle testing, and corrosion testing, and the need for the development of new, platable plastics.

(author)

INTRODUCTION

In a previous presentation before this Society,[1] an attempt was made to describe the present understanding of how plated metals corrode and how this corrosion may be controlled. It was pointed out that metals do corrode but that the durability may be extended significantly by controlling the rate of corrosion. Thus, duplex and triplex nickels, with differing amounts of included sulfur, provide for a lateral movement of corrosion and delay penetration to the basis metal. Also, microcracked and microporous chromium, which provide a very large number of attack sites, effectively distribute the anodic (corrosion) current over a relatively large area, thereby decreasing the current density and the penetration at any given site. These approaches have led to greatly enhanced durability of plated steel and zinc die cast parts.

In discussing the GMR Electrolytic Corrosion (EC) Test, it was pointed out that this test has the capability of predicting, in about two minutes, the durability to be expected of plated surfaces exposed for one year in the Detroit area. It was mentioned that difficulties had arisen in applying this test to plated plastics. While progress has been made, problems remain principally because the basic material is a nonconductor. This problem will be discussed in detail later on.

The problem of thermal cycling was also mentioned wherein concern was expressed over the temperature ranges being specified, but more importantly, over the rates of change of temperature being employed. Some information and some pertinent questions about this test procedure will also be presented.

In spite of the many advances made recently in the plating of plastics, it is the purpose of this presentation to identify and discuss the problem areas which still exist, and to propose some means by which the maximum amount of information may be extracted from test programs carried on by both suppliers and users of plated plastics. In particular, this paper discusses the examination of polymer surfaces, adhesion testing, thermal cycle testing, corrosion testing, and the correlations and interactions among these tests.

EXAMINATION OF POLYMER SURFACES

The decorative and functional properties of electroplated plastics depend largely on retention of adhesion of the deposit to the polymer surface. The well-known effects of molding parameters on the adhesion of deposits indicate that the composition and structure of the polymer surface exert a controlling influence on the durability of plated plastics.[2,3,4] Characterization of such surfaces is difficult. Their properties are those of surface zones of macromolecules which are very probably different from bulk properties. The difficulty is aggravated since the elementary unit, the macromolecule, has ill-defined composition, structure and size. The arrangement of these units at the surface is believed to be rather random.

A. Optical Techniques

To study the composition of such surfaces, techniques such as multiple attenuated response (MATR) spectroscopy must be employed. Interpretation of the spectra is as yet difficult. The effects of the molding processes on the success or failure of plating processes indicate that the physical structure should be examined also. This can be done conveniently with optical and electron microscopy. Optical microscopy is suitable if structural features with dimensions greater than a few microns are present, and topographical variations on the order of a tenth of a micron can be studied with interference microscopy. The utility of these techniques is illustrated by the results of an exploratory study made during an evaluation of an experimental process for plating on polypropylene.

B. Study of Polypropylene Surfaces

In this study, small coupons were cut from injection molded polypropylene (Profax 6523, Hercules, Inc.) plaques. The same area on each coupon was examined before treatment and after each step of the process, using a metallograph and an interference microscope. The process consisted of a solvent soak, chromic-sulfuric acid conditioning, stannous chloride sensitization, palladium chloride activation, and electroless nickel plating. From these examinations, it was concluded that:

1. Most complete and uniform coverage by the nickel was obtained only when the polypropylene surface was aggressively and uniformly attacked by the conditioner with the formation of cracks and fissures, as shown in Figure 1.
2. Initiation of the electroless nickel deposit occurred preferentially in surface fissures and cracks resulting

from attack by the conditioner. Some typical results are shown in Figure 2.

3. The solvent soak promoted more uniform attach by swelling the plastics (and perhaps by dissolution of some surface material) to make susceptible sites more accessible to the conditioner.

4. Structural inhomogeneities, attributable to inhomogeneous composition of the polymer and to the molding process, were observed; these can have appreciable effects on response to conditioning and, subsequently, initiation of the nickel deposit.

5. Under the conditions employed in this study, metalpolypropylene adhesion appears to be purely mechanical.

C. Implications

The conclusions reached from this exploratory study of the effect of one process on a single type of polypropylene molding cannot, of course, be considered generally applicable to all plated plastics. The results do indicate the desirability of such work and where more comprehensive study is needed particularly to confirm the apparent dependence of coverage by the initial electroless deposit on the type of surface resulting from the conditioning step of the process. The most interesting aspect is, perhaps, that the electroless nickel deposit is initiated preferentially at sites in fissures and cracks.

When the as-molded surface was removed by microtoming, a very large number of uniformly spaced cracks resulted from the conditioning treatment. Complete coverage of the surface was achieved with a two-minute electroless nickel deposit, while on the as-molded surface, equal coverage requires at least five minutes.

The limitations of optical microscopy to such a study are obvious; electron microscopy is indicated. The recent work of Marton and Schlesinger[5] is of interest since a correlation is indicated between hydrophobocity and the density of sites where electroless deposition initiates.

Other techniques for study of surfaces must be considered since reliance on one method is rather dangerous. For example, radically different conclusions about the mechanism of adhesion of deposits to ABS surfaces resulted from the work of Heymann,[2] who relied on electron microscopy, and Saubestre, et al,[6] who used optical microscopy extensively.

ADHESION TESTING

Adhesion tests for plated coatings on metal substrates have been attempted for a number of years but little success has been achieved. Adhesion has not been a real problem, and most efforts have been toward a heating of the part followed by quenching for studying electrodeposits on such substrates as aluminum and magnesium. Results indicated the efficacy of the processing steps.

A. The Peel Test

A widely used adhesion test for plated plastics is the peel test. The question that arises is the correlation of the data with other factors involved in producing an acceptable part. In the past few years, improvements in plated plastics can be seen by comparing early data, three to five lb/in. peel strength for plated ABS, to recent results of 10-15 lb./in. for the same general systems. Part of this increase can be attributed to the conditioners now available, and part to the changes in electroless deposition procedures. It is probably difficult to separate these effects, but efforts should be made to do this. If a conditioner-electroless deposit combination is known to be good, effects of modifying either the conditioner or the electroless plating process should be determined separately.

B. Observation of Surfaces After Testing

After peel testing, the surfaces of the plastics and the electroless deposit in contact with each other should be examined.

The peel test is usually performed after the panels have been aged for 48 hours. Results show that aging generally produces higher values of adhesion than do freshly plated samples. One possible cause for this is that moisture is driven out of the interface through minute pores in the plated coating. More work is needed to explain this aging effect fully, as elimination of the 48-hour delay time is desirable.

It has been noted that plated ABS surfaces with high adhesion values are lighter in color and have discrete particles of metal adhering to the plastics exposed during the peel test. The interface side of the metal coating is usually more metallic in color and has particles of plastics adhering to the surface. When low adhesion values are obtained, the plastics is darker or more like the original color and the metal has what appears to be an oxide film. Changes in surface textures are very subtle and difficult to determine, even with the aid of a microscope.

Observations of these items may prove fruitful in determining the action of the preplating steps on the plastics surface and the number of initiation sites of the electroless deposits. Correlation of these observations with variations in peel-test results could be of value in understanding adhesion.

C. Peel Testing of Panels and Parts

One way to correlate results from panels and parts is to perform peel tests on both. Some parts have insufficient flat areas for this, but others do have enough to pull narrow strips. The standard test has been to use strips one inch wide, but this is not always necessary. To illustrate, ABS panels were plated, with electroless copper plus two mils of electrodeposited acid copper. An Instron Universal Tester was used to peel test the one in. strip varying regularly from one to 1/4 in., Figure 3. Peel test results are shown in Figure 4. Note the essentially horizontal line for the one in. strip and the regularly decreasing line for the decreasing width. To check this further, strips having widths of 1/4, 1/2 and one in. were pulled on another set of panels plated similarly. The strips were delineated by etching (with $FeCl_3$) the separation lines imprinted on a photoresist. The test panel is shown in Figure 5, and the results in Figure 6. When the widths of the test strips were measured accurately, the results on a one in. equivalent basis are within 3 per cent (± 0.5 lb/in.) These data show that narrow strips can be used for peel testing and that the test can be performed on at least some parts as well as on panels.

D. Reporting of Adhesion Test Results

An area that needs improvement in providing useful information is the reporting of results of adhesion tests. All too frequently the literature gives peel test values without stating the plating system applied, e.g., the type of electroless deposit and the electrodeposited coating; all too often, the type of equipment used, e.g., an Instron Universal Tester, or some other device, is not mentioned. If full information is provided, the results of any test can be compared to those of other tests. It is highly recommended that adhesion test reports specify the type and thickness of the metals deposited, and describe the equipment and procedure used to measure the adhesion values. What is vitally needed is standardization of the test method.

THERMAL CYCLE TESTING

The thermal cycle test continues to be used for evaluating the physical durability of metal-plated plastics parts and panels, and the adhesion of plated metal layers to highly curved parts. Although much space has been devoted to technical and promotional articles regarding plated plastics, relatively little has been published about the thermal cycle test itself. The following discussion is devoted to some points which arise when evaluating thermal cycle test results or when studying proposed thermal cycle test procedures.

A. Criteria

Little has been published about criteria for evaluating parts after thermal cycle testing. Carter[3] discussed three categories of defects observed: plastics defects manifest as warpage; plastics defects as sinks (local shrinkage without plating fracture), folds, or waviness, and bubbles; and plating defects as cracking, peeling, and blistering or loss of adhesion.

A fourth category can possibly be established for some results observed in this laboratory where a few hairline or microcracks develop after thermal cycling. There appears to be no loss of adhesion, the crack penetrates the metal layer completely, and after stripping the metal, the trace of the crack may be just barely discernible in the plastics. The cracks are straight or only slightly curved and do not branch. The same appearance has been observed on parts which others have represented (rather optimistically) as having passed the test. Does this microcracking constitute failure? Further, does the development of voids over which the metal does not crack or blister, as mentioned by Carter[3] and observedhere, also signal failure?

B. Test Sequence

Thermal cycle testing usually calls for a high temperature of 180°F (sometimes 185°) followed by cooling to -20°F. The reason generally given for this order is that the part undergoes some stress relief and some further improvement of adhesion by artificial aging as the temperature increases. Should some parts be subjected to a reverse sequence? Should an alternation of sequence be used? Saubestre[6] used an alternate sequence in some thermal shock tests and concluded in general that no great difference was observed between these and the thermal cycle test.

C. Test Temperatures and Rate of Heating or Cooling

In connection with thermal cycle testing, the question of temperature extremes arises. One recommendation[7] calls for an upper temperature of 180 F and a lower temperature of -20°F. ASTM Committee B-8[8] has called for four classes of application of the thermal cycle test. Among these, the "outdoor" application calls for test temperatures of -40° and +180°F, while the "high-temperature" application calls for -40° and +200°F. The ASEP Industrial Standards Committee[9] has gone on record as disapproving these temperatures as being too severe and suggests instead that a lower temperature limit be established for a particular test with application of a 150°F range to the upper temperature. As of this writing, these differences have not been resolved.

A further question, perhaps of greater importance, concerns the rate of heating and of cooling in the thermal cycle test. Carter[3] observed an initial heating rate on surfaces of his plated ABS samples (equipped with thermocouples) of about 2800°F/hr. in an oven set at 200°F. In cooling the samples in a deepfreeze set at -40°F, he observed an initial cooling rate of -1260°F/hr.

Using plated ABS panels equipped with thermocouples, an initial cooling rate of -540°F/hr. in a deepfreeze set at -20°F has been observed in this laboratory. As a check on service-like conditions, more thermocouple-equipped panels were mounted on an automobile which was then moved from outdoors (at 70°F) into a cold test room at -20°F. The observed initial cooling rate was -80°F/hr., and the samples took 17 hours to attain -20°F on continued exposure in the cold room. The discrepancy between the cooling rates in deepfreeze sample exposure and the more service-like exposure indicates strongly that more work must be done on the temperature extremes and cooling/heating rates to attain a reasonable correlation to service.

D. Extent of Cycling

The recommendation quoted before[7] also calls for a total of three thermal cycles for specification testing. In some of his work, Saubestre[6] used 15 cycles as a criterion. Later, he indicated that much more information is needed before a specification for a given number of cycles can be made.[10] On the other hand, Carter[3] started his work using 11 cycles and found later that six cycles yielded sufficient information. These results reinforce the question of correlation of thermal cycle testing to service exposure and point up the uncertainty of the extent of cycling necessary to assure confidence in the quality of a plated part.

E. Constraint

In the references concerning thermal cycle testing,[3,6,10] no statements were made concerning whether the samples were tested as loose parts or were fastened to some kind of rack. The effects of internal stress of the part on thermal cycle results have been noted.[3,6] It stands to reason that external stress resulting from constraint by mounting of parts in service must be reasonably simulated if better service correlation is sought. This may be even more important in the case of exterior plated trim which is to be cemented at all points of contact to the automobile. Figure 7 illustrates one example of how such testing may be carried out.

F. Further Interpretation of Results

In addition to evaluating durability and adhesion, can thermal cycle test results be used to determine whether poor performance results from process or from system failure? By process failure is meant improper operation regarding time, temperature, solution condition (cleanliness), or rinsing procedure. System failure means improper application or inadequacies of the metal-plating system for the particular plastics being processed. Roobol[11] in discussing Saubestre's[10] work, shows that thermal cycle failure can be related to the design of the part and to the plating system used, and that both of these factors must be taken into consideration when interpreting test results.

G. Commentary

It is to be understood clearly that answers to the many questions raised are necessary but not sufficient to establish proper practice and interpretation of the thermal cycle test. In addition to uncertainty about the test itself, it is necessary to consider the interactions with other tests to establish meaningful correlations.

CORROSION TESTING

While it is extremely desirable to study the entire cycle life of plated plastics parts in service, it is not a practical method for continuous control testing. Thus it is necessary to depend upon accelerated corrosion tests.[12,13,14]

Exploratory CASS testing was done on plated ABS panels, the primary concern being the observation of characteristic developments in the test and in a general comparative appraisal of an acid copper (0.5 mil)-duplex nickel (1.0 mil)-chromium (0.01 mil) system over an initial deposit of either electroless copper or electroless nickel.

It is recognized that microporous chromium is now starting to be used on plated plastics but, for the purpose of this work, conventional chromium over duplex nickel was chosen to facilitate the development of green corrosion products which apparently has been associated with CASS test results. It seemed desirable to trace the origin of the green product by collecting and analyzing for the copper and nickel content, the CASS runoff solutions collected from the exposed panels, and to identify the product itself by X-ray fluorescence and spectrographic analysis.

CASS test cabinet conditions were rigidly controlled to meet all specifications,[15] but the time of exposure was extended from the customary 22 hours to a total time of 96 hours to develop substantial failures for chemical analysis and to obtain obvious differences. Observations and runoff solution collections were made at intervals of eight and 16 hours throughout the test. Chemical analyses were made on the entire volume of solution collected for each panel at the end of the test.

Controls for the test were four steel panels plated with a cyanide copper strike and the same acid copper-duplex nickel-chromium plating system used on the plastics panels. An unplated ABS plastics panel was also exposed, and the collections from these panels were also analyzed.

The following observations have been made:

1. The plated plastics panels were covered extensively with the green corrosion product, the plated steel panels were rust covered, and the unplated plastics panel was unchanged. The green corrosion product was insoluble in water and required scraping for removal.

2. All plated plastics panels developed either blisters or crater-type pits in totally penetrated corrosion sites. Blisters were characteristic of the panels plated initially with electroless nickel while the crater-type pits were associated with the panels plated initially with an electroless deposit of copper.

3. Chemical analyses of the runoff solutions showed an amount of copper equal to that introduced by the CASS solution itself, and nickel content ranging from 0.04 to 0.31 mg/ml of solution collected. X-ray diffraction analysis of the green corrosion product indicates that it is a mixture of sodium chloride and copper hydroxy chloride, $Cu_2(OH)_3Cl$, but further analytical work is required for substantiation.

4. The progression of corrosion (rates of penetration) on plated plastics is normal with respect to the copper-nickel-chromium plating system used.

A. Electrolytic Corrosion (EC) Testing

As mentioned earlier in the paper, the Electrolytic Corrosion (EC) Test[16] has been applied to the corrosion testing of plated plastics but with inconclusive results.

For plated metal substrates, the test has been calibrated to reproduce, in two minutes, a service exposure of one year on Detroit's streets. Because the test is electrolytic, the initial current density can be used as an indicator of the porosity of the chromium later. This information is an important first step toward understanding the corrosion behavior of particular parts made from metal.

On metal substrates, totally penetrated sites carry current continuously, and the current rises proportional to the increase of the area of the anodic (corrosion) sites and to the number of sites developed during electrolysis. The trend is shown in Figure 8 and also in this figure is shown the current-time curve on a plated plastics substrate. It is tempting to assume that the rate of penetration of the metal layers is the same as it is on metal substrates, but is it? Is the two minutes $\approxeq$ one year service factor still valid? Certainly, the plastics has altered in some unknown manner the progress of the corrosion process.

Hepfer[17] has reported the results of the application of CASS, Corrodkote, and service testing of ABS panels plated with 25 different deposit systems. Replicate panels of these 25 systems were also tested in this laboratory using the EC test, and an attempt was made to rank the performance of the systems as indicated by the change from initial to final current. Results agreed favorably, in most cases, with rankings established by the other tests, but some familiar EC test characteristics were changed perceptibly.

Perhaps the most significant change was in the corrosion pit shape which developed in totally penetrated sites and the effect this change had on the current during the test. Figure 9 shows the extension of the affected area beyond the nucleus of the pit; the entire area is no longer conductive. It is readily apparent that this observation must be related to the characteristics of corrosion activity which takes place in service. Obviously, many more tests must be conducted to correlate the EC test with serviceexposure, and a great deal more service exposure data must be obtained before there can be any certainty about the durability of plated plastics used for exterior automotive trim.

CORRELATIONS AND INTERACTIONS AMONG TESTS

A. Peel Test and Thermal Cycle Test

There is very little in the literature concerning the correlation between these two tests in spite of the fact that both are aimed at determining adhesion. Peel tests are usually performed on flat panels while both panels and parts are thermal cycled. Since it has been shown that strips as narrow as 1/4 in. can be used for the peel test, then at least some parts, depending upon their geometry, can be both peel tested and thermal cycled. More attention must be paid to this correlation.

B. Acetic Acid Test and Thermal Cycle Test

The acetic acid test is used to develop, on the surfaces of parts molded from ABS, whitish areas which are assumed to be stressed areas. Are these indeed stressed areas? Saubestre[6] has noted that such areas correlate with failure in thermal cycling and states that the stressed areas are susceptible to overconditioning. To illustrate this correlation, some ABS molded lamp housings were selected for acetic acid testing and for plating. Thermal cycle test results on the plated housings (Figure 10) show failure that corresponds very well to the whitish areas developed in acetic acid.

Schwartz and Hartley[18] indicated that the whitish areas are the result of etching by the acetic acid followed by surface cracking during stress relief. The exact nature of the whitish areas needs to be determined.

This test is applicable when ABS is being used, but a similar test needs to be devised for polypropylene.

C. CASS Test and Thermal Cycle Test

While Carter[3] concluded that combined CASS testing and thermal cycle testing on the same samples showed no advantage over separate testing, results obtained in this laboratory indicate that there is a difference depending upon the use of electroless copper or electroless nickel. The sequence of CASS testing before or after thermal cycling showed no particular influence on panels having an electroless copper base layer. With an electroless nickel base, however, the sequence of CASS testing before thermal cycling seemed to increase the extent of blistering to areas not penetrated by corrosion to give an interconnecting area of massive adhesion loss, whereas blisters from the opposite sequence did not interconnect. From these observations, it is quite clear that the CASS-thermal cycle interaction is not understood and requires much more work. This is especially important because of the corrosion that will occur in service.

NEW PLASTICS NEEDED

Finally, perhaps the greatest challenge facing the suppliers of plastics is to provide new materials which have all the desirable characteristics of a platable plastics.

To date, some parts made of unfilled ABS suffer from too great a thermal coefficient of expansion and all too often cannot pass the thermal cycle test. Parts made from glass-filled ABS can pass the test, but their appearance is not acceptable because of the "bumpiness" resulting from the protruding ends of the glass fibers. These observations suggest that the role of "composites" should be explored vigorously.

It has been found impossible to plate, at least reproducibly, all grades of ABS and polypropylene. Indeed, for each material, only a limited number of grades can be plated successfully using at best only one or two proprietary processes. What must be recognized is that, at the current state of development, only "special grades" of these materials can be plated reproducibly.

What is needed is new polymers. The modification of shelf items to provide so-called "platable grades" of plastics has not proved to be completely satisfactory. Certainly this requirement will tax the ingenuity of the polymer chemist, but herein lies the real challenge.

ACKNOWLEDGMENTS

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providing some of the illustrations; and to Messrs. G. Froczila and T. E. Gardziola, of the Manufacturing Development Section of Manufacturing Staff, General Motors Corporation, for molding and plating some of the samples.

REFERENCES

1. Beacom, S.E., "The Durability Aspects of Plated Plastics", RETEC, Soc. of Plastics Engineers, Hartford, Conn., Nov. 17, 1966.
2. Heymann, K., "Surface 1966" (Ed. by N. Ibl, K. M. Oesterle, and A. L. Saboz), p. 97, Forster-Verlag, A.G., Zurich (1967).
3. Carter, V.E., Trans. Inst. Metal Finishing, 46, 49 (1968).
4. Marbon Chemical Div., Borg-Warner Corp., Tech. Report P-131.
5. Marton, J.P. and Schlesinger, M., J. Electrochem. Soc., 115, 16 (1968).
6. Saubestre, E.B., Darney, L.J., Hadju, J. and Bastenbeck, E., Plating, 52, 982 (1965).
7. Marbon Chemical Division, Borg-Warner Corp., TM 253-67A.
8. American Soc. for Testing and Materials, Committee B-8, Subcommittee II, Section M, Group 4, Jan. 31, 1968.
9. American Soc. for Electroplated Plastics, Industry Standards Committee, Discussion Group B, Feb., 1968.
10. Saubestre, E.B. and Hadju, J., Plating, 55, 51 (1968).
11. Roobol, N.R., Plating, 55, 476 (1968).
12. Saur, R. L., Plating, 48, 1310 (1961).
13. Saur, R.L., and Basco, R.P., Plating, 53, 370 (1966).
14. Saur, R.L., and Basco, R.P., Plating, 53, 981 (1966).
15. General Motors Specification 4476-P.
16. Saur, R.L. and Basco, R.P., Plating, 53, 35 (1966).
17. Hepfer, I.C., Hampel, K., Timmen, R.J. and Boehm, D.R., Plating, 55, 584 (1968).
18. Schwartz, E. and Hartley, J.C., SPE JOURNAL, 23, 110 (1967).

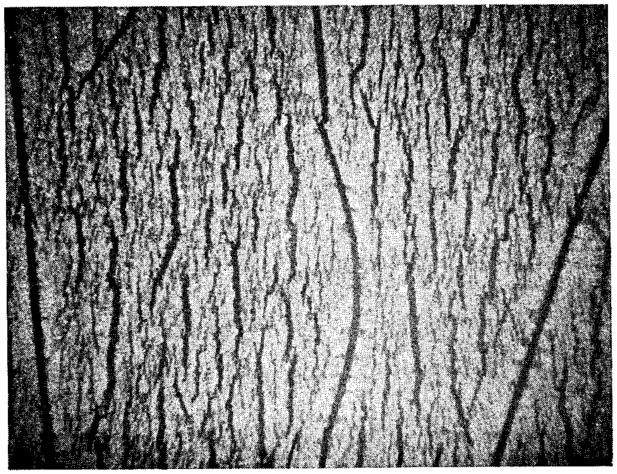


FIGURE 1: Cracks and fissures in polypropylene after 15-min. etch in hot chromic-sulfuric acid solution. (75X, dark field)

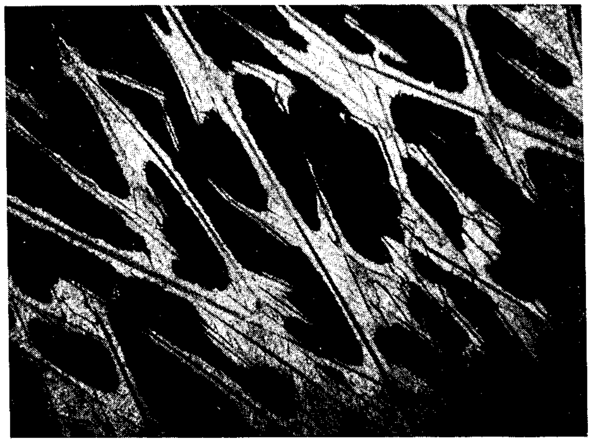


FIGURE 2: Spread of electroless nickel deposit from cracks in surface of a polypropylene sample. (Nickel deposit appears as light shade, 60X, dark field.)

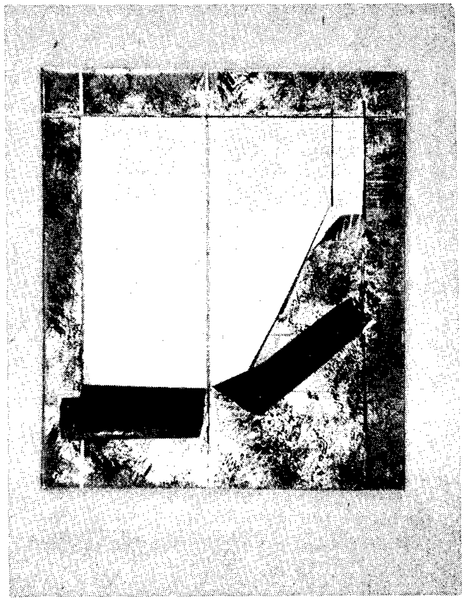


FIGURE 3: Peel testing of a 1-in. strip and a strip varying from 1-in. to ¼-in.

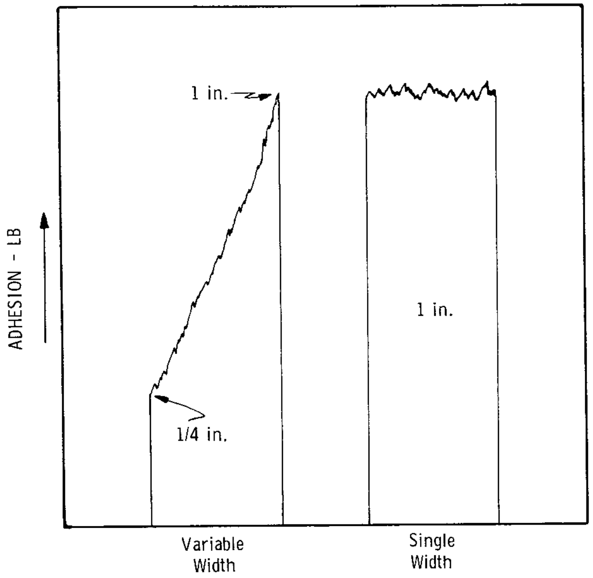


FIGURE 4

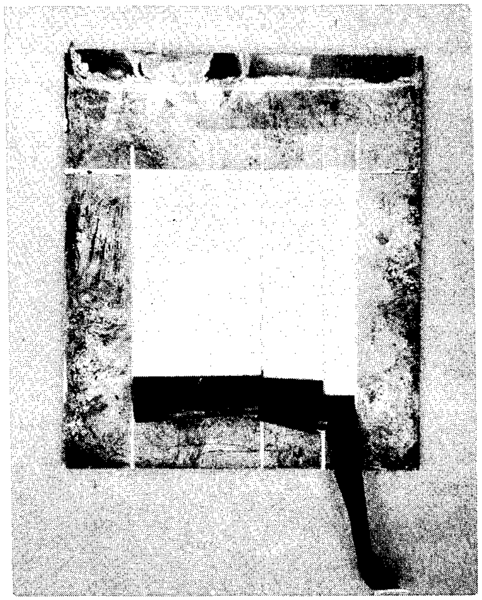


FIGURE 5: Peel testing of 1-in., ½-in., and ¼-in. strips.

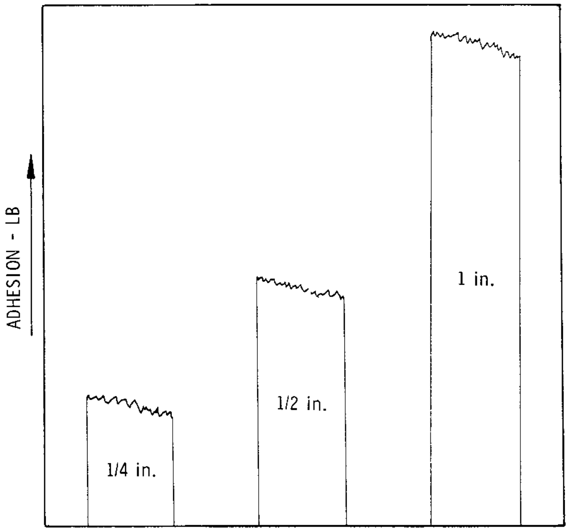
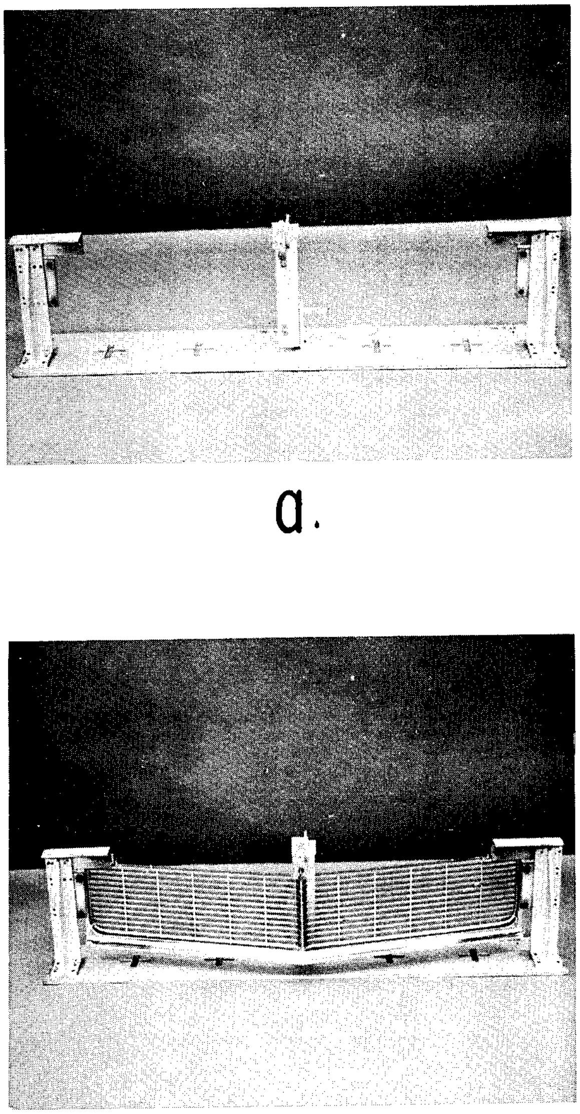


FIGURE 6



a.

b.

FIGURE 7: Thermal cycling of plated parts under constraint.
a.) Fixture b.) Fixture with part in place.

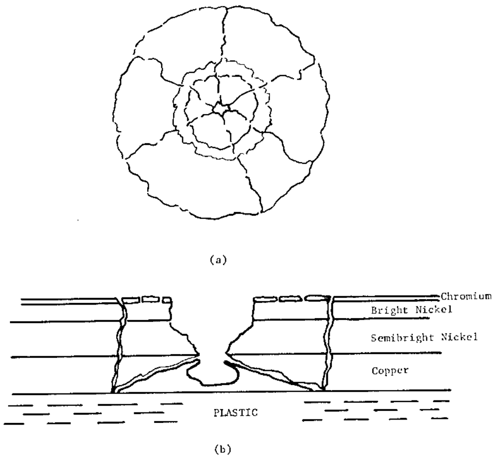


FIGURE 9

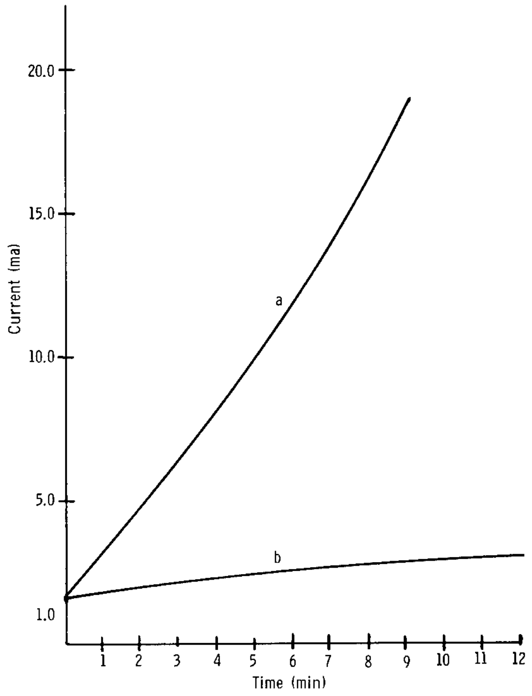


FIGURE 8

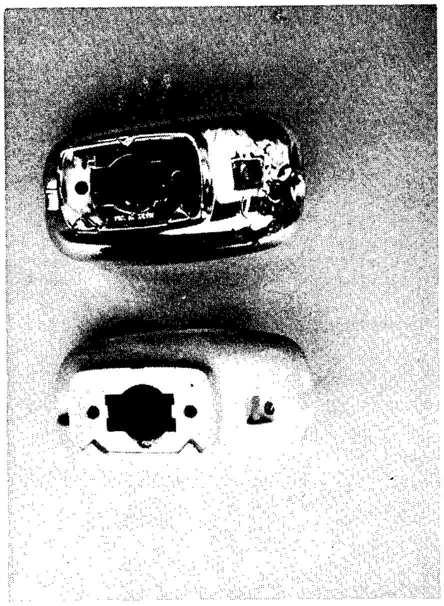


FIGURE 10: Correlation of stress location and thermal cycle failure.

INITIATION FEE MUST BE ATTACHED FOR PROCESSING.

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I hereby make application for ☐ admission into ☐ reclassification within ☐ reinstatement in the Society of Plastics Engineers, Inc. in the grade of membership indicated below for which I believe I am qualified. (See instructions or reverse side.)

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☐ Senior Member	$10.00	$20.00	$17.50
☐ Member	10.00	20.00	17.50
☐ Affiliate Member	10.00	20.00	17.50
☐ Student Member	None	5.00	5.00

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3. ______ Address ______

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From	To				
				Total Education Experience Credits	

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Dates				Give your title, name and location of employer, and name of immediate superior for each position. List in chronological order. Describe duties fully and state briefly any important engineering work you have done in in each position. If space is not sufficient, use a separate sheet.	Time in years and months
From		To			
Mo.	Yr.	Mo.	Yr.		
				Total qualifying years of experience.	
				Total education and qualifying experience credits.	

I certify that the statements made in this application are correct. I agree, if elected, to be governed by the Constitution and By-Laws of the Society, and to promote the objective of the Society.

NATIONAL CREDENTIALS COMMITTEE USE ONLY

Approved (Signature) Date

Approved (Signature) Date

______ Date of Application

______ Signature in ink.

COMPLETING THE APPLICATION

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Membership grades are based on experience credits which are earned as follows:

1. **Experience credits earned for education.**

   Doctorate in science or engineering subject: **6 credits**
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   Other degree in non-science or non-engineering subject: **2 credits**

   Maximum credits allowable for education shall be six (6).

   When filling in the "Statement of College Work" on the reverse side of this application, please place the corresponding number of credits earned in the right-hand column.

2. **Experience credits** for qualifying experience in plastics or plastics engineering are earned at the rate of one (1) per year, e.g. 5½ years of qualifying experience = 5½ credits. *Please detail carefully the engineering skill required for* ***each position*** *to help the Credentials Committee judge experience as "qualifying."*

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When you have determined the number of credits which you believe you have earned consult the following membership grade requirements. Indicate on the reverse side the grade of membership for which you believe you are qualified.

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Member	Minimum of six (6) experience credits
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6. ☐ Fabricated Metal Products and Housewares
7. ☐ Finished Apparel Products
8. ☐ Food and Tobacco Products
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15. ☐ Leather and Leather Products
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17. ☐ Plastics Custom Molders, Extruders, Laminators, and Fabricators
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20. ☐ Plastic Machinery

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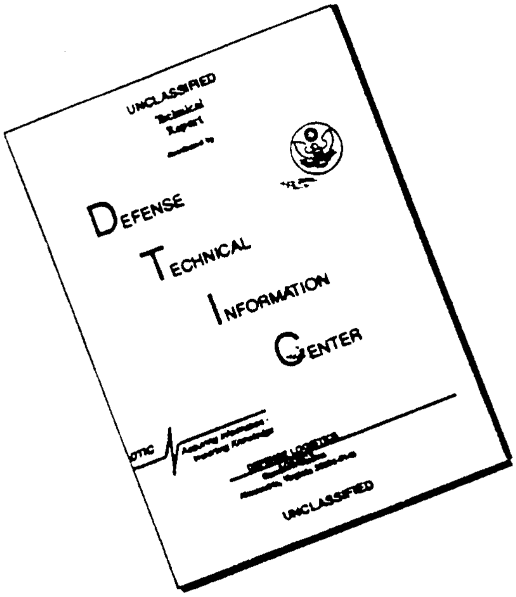

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