

## Studies on Tack of Pressure-Sensitive Adhesive Tapes: On the Surface Contamination by Adhesive Mass After Peeling

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### Synopsis

The presence of adhesive residue on the surface of various adherends after peeling has been confirmed using a tracer technique. Adhesive bonding is found to break by a cohesive mechanism, although the unbonding process seems apparently to be due to inter-surface failure. This result supports the concept for adhesive bond breaking proposed in the preceding paper: The unbonding proceeds from the viscoelastic deformation of the adhesive mass around the wetted spots on the surface. As the number of spots in a unit area is controlled by surface energy, the tack value is dependent on the critical surface tension of the adherends.

### INTRODUCTION

In the preceding paper<sup>1</sup> it was reported that the tack values of pressure-sensitive adhesive tapes are dependent on the critical surface tension  $\gamma_c$  for adherends, and the parabolic curves with a maximum were obtained from the plot of tack values versus  $\gamma_c$ . In order to explain the control of the tack values by  $\gamma_c$  of the adherends, a mechanism was proposed for adhesive bond breaking. Accordingly, bond breaking is attributed to the deformation of the adhesive mass around the very minute spots on the surface where substrate and adhesive interact. To prove this argument, it is necessary to show the presence of adhesive residue on the surface.

For the detection of the pick-off on the surface, application of electron microscope,<sup>2</sup> contact angle measurement,<sup>3</sup> and dyes<sup>4</sup> are reported in the literature. However, a tracer method using radioactive adhesives is best for the purpose because of its high sensitivity. This paper deals with the estimation of pick-off on the surface using radioactive adhesives.

### EXPERIMENTAL

Labeled pressure-sensitive sheets were cut into rectangular pieces (50 × 60 mm), and a piece was put on the surface of a plastic plate under constant conditions (5-kg load at 20°C). After leaving a sample in phase for a fixed time, the adhesive sheet was peeled off at a constant rate of 300

mm/min, and the residual radioactivity on the plate was directly measured using an end-window GM counter tube.

The pick-off on the probe after butt tensile tack measurements was, however, difficult because the total adhesive area was too narrow (5 mm diameter) to measure the residual radioactivity using the end-window counter tube. In such a case, the changes in contact angle for pure water were followed.

## Materials

### *Natural Rubber-Based Adhesive*

In this case, the tackifier was labeled using isotope. Glycerol-1-<sup>14</sup>C, 0.1 mCi, was diluted with 3.0 g of inactive glycerol and esterified with 30.0 g of hydrogenated rosin (Hercules' Staybelite resin, A.V., 160, softening point, 65°C) in nitrogen atmosphere at 280°–290°C for 9 hr. Yield, 32 g; A.V., 21.7; softening point, 68.5°C.

The mixture of 15 g of labeled hydrogenated rosin ester and 22.5 g of natural rubber (ML<sub>100°C</sub>, 50) was dissolved in 200 ml of *n*-hexane. The solution of natural rubber-based adhesive thus prepared was coated on the biaxially drawn poly(ethylene terephthalate) film (Torey's Lumirror No. 25) and dried to prepare an adhesive sheet. The thickness of the dry adhesive layer was controlled within 0.03 ± 0.005 mm.

### *Acrylic Adhesive*

As described in the preceding paper,<sup>1</sup> the copolymer consisting of 64% of ethyl acrylate and 36% of 2-ethylhexyl acrylate was used. Labeled ethyl acrylate was used to prepare radioactive acrylic adhesive.

Ethanol-1-<sup>14</sup>C, 0.05 mCi, was diluted with 4.6 g of inactive ethanol and esterified with 10.0 g of acryloyl chloride in 40 ml of dry ether in the presence of 14.0 g of *N,N*-dimethylaniline under an atmosphere of nitrogen. After the reaction, the mixture was washed with dilute H<sub>2</sub>SO<sub>4</sub> followed with water. The oil layer was separated and dried overnight over anhydrous sodium sulfate and then distilled. Yield was 10 g (99%); bp, 100°C; *n*<sub>D</sub><sup>25</sup>, 1.4039. In the literature,<sup>5</sup> bp, 98°–100°C; *n*<sub>D</sub><sup>25</sup>, 1.4037.

Adhesive was prepared by the copolymerization of 4.3 g of labeled ethyl acrylate with 2.4 g of 2-ethylhexyl acrylate in 6.7 ml of ethyl acetate in the presence of 0.01% of benzoyl peroxide. Copolymerization was carried out in a glass tube sealed under vacuum at 60° ± 0.2°C for 30 hr, ( $[\eta]$ , 0.7 at 30°C in ethyl acetate).

The copolymer obtained was directly coated on biaxially drawn poly(ethylene terephthalate) film (Torey's Lumirror No. 25) and dried strictly to prepare adhesive sheets. The dry adhesive layer was controlled within 0.03 ± 0.005 mm.

### Measurement of Radioactivity

Measurement of radioactivity was carried out using an alcohol quenching GM tube made by Riken Keiki Fine Instrument Co., and dekatron scaler capable of a maximum counting rate of 20,000 cps.

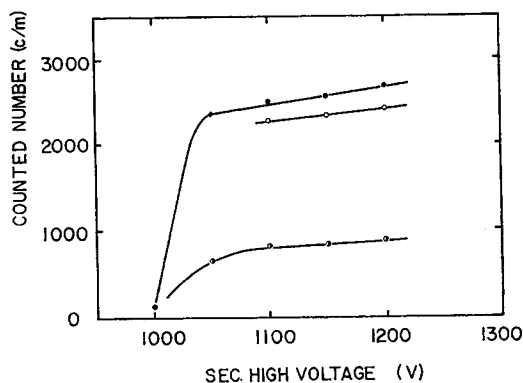


Fig. 1. Plateau characteristics of GM tube: (○) standard sample with radioactivity counted to be 2340 c/m at 1150 V; (●) 2550 c/m; (●) 830 c/m at 1150 V.

Figure 1 shows the plateau characteristic for the GM tube. Since the anode voltage for the GM tube was controlled within  $1150 \pm 2.5$  volts using a vacuum-tube voltage regulator, the maximum range of counted value is within  $\pm 0.2\%$ , as shown in Figure 1. The counted number for activity is the average of three to five measurements, and ranges of these values were within about  $\pm 5\%$ .

A radioautograph was taken using Sakura x-ray film G.H.  $^{14}\text{C}$ -labeled tape was fixed on a plastic plate under a 5-kg load, and after 24 hr, the tape was peeled off the plate at a rate of 300 mm/min. The x-ray film was then put on the surface of the plastic plate. After 50 days of exposure, the x-ray film was developed.

### Contact Angle

Changes in contact angle on the surface of the plastic probes were estimated by direct observation of drops of water using a contact angle goniometer made by Erma Optical Works, at 45% R.H. and 20°C.

### Tack and Peel Force Measurements

A Polyken probe tack tester and a Shopper-type tensile tester were used for measurements of butt tensile tack and 180° peel force, respectively.<sup>1</sup>

## RESULTS AND DISCUSSION

## Adhesive Selectivity

Figures 2 and 3 show the relationship between tack values or peel forces and  $\gamma_c$  of adherends for natural rubber based and acrylic adhesives, respectively. The tack values were controlled by  $\gamma_c$  of the adherends, and the parabolic curves with maxima were observed in every case as reported in the preceding paper.<sup>1</sup> The maxima were found at  $\gamma_c$  values between 33 and 39 dynes/cm: these are quite similar to those for adhesives used.<sup>1</sup>

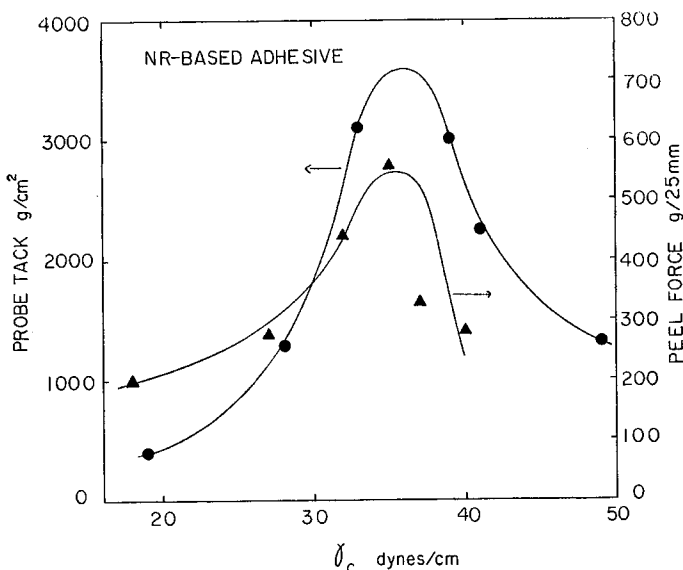


Fig. 2. Relationship between tack value and surface energy for adherends, at 20°C. The probes and plates were the same materials as described in the preceding paper,<sup>1</sup> except for probe prepared from epoxy resin, for which  $\gamma_c$  of 49 dynes/cm was determined from plot of  $\cos \theta$  vs. surface tension for aqueous solution of dipropylene glycol: (●) probe tack; (▲) peel force.

To explain why the tack value is controlled by  $\gamma_c$  of the adherends, it is proposed that the bond breaking proceeds from the viscoelastic deformation of the adhesive mass around the wetted spots on the surface of the adherend.<sup>1</sup> As the number of spots in the unit area will be dependent on the wettability of the substrate, the tack value is controlled by  $\gamma_c$  for the substrate.

Therefore, it is necessary to show the presence of pick-off on the substrate as proof of cohesive bond breaking around the minute spots.

## Contamination on the Surface of Adherends

Tables I and II indicate the changes in radioactivity on the various plastic plates before and after application of  $^{14}\text{C}$ -labeled adhesives composed of natural rubber/hydrogenated rosin ester and of acrylic copolymer, respectively. In every case, residual radioactivity was counted for polystyrene and poly(methyl methacrylate): these polymers were found to give considerably high tack values. Therefore, in these materials the presence of pick-off and cohesive failure was confirmed, although the un-bonding observed is apparently due to intersurface failure.

These residual activities disappeared after washing of the surface using distilled *n*-hexane. This indicates that the contamination is limited only to the surface. Amounts of pick-off can be estimated to be ca. 0.2% of

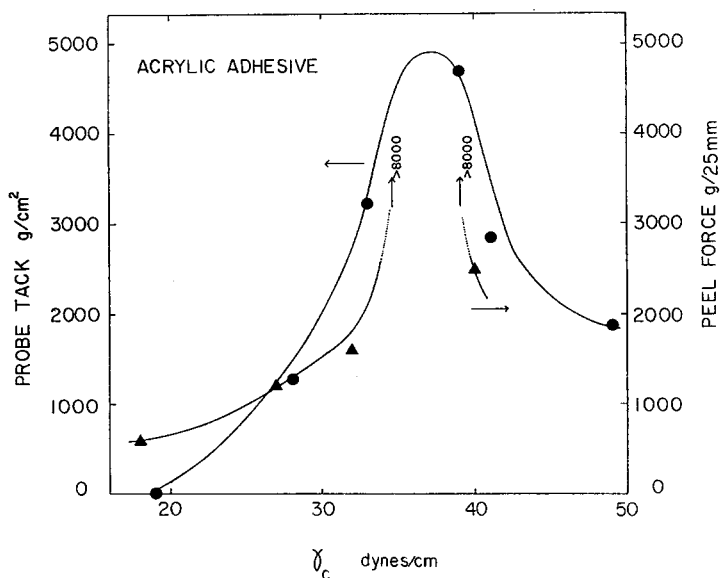


Fig. 3. Relationship between tack value and surface energy for adherends, at 20°C: (●) probe tack; (▲) peel force.

total amounts of adhesives from the ratio of activities for adhesive surface and the surface of plastic plates after peeling. However, this value should actually be much lower because of the effects of the thickness of the adhesive layer.

As described in the preceding paper,<sup>1</sup> it is necessary to keep the adhesive tape in a fixed state for a very long period in order to attain complete contact, because of the high viscosity of pressure-sensitive adhesive masses. Table III shows the changes in residual activities after long contact time. Radioactivities were detected after peeling for all plastic plates except Teflon, nylon, and stainless steel.

TABLE I  
Changes in Radioactivity Before and After Application of Labeled  
Adhesive Composed of Natural Rubber and Hydrogenated Rosin Ester<sup>a</sup>

Substrates	Radioactivity, cpm				Contami- nation
	Surface of adhesive	Before application	After peeling	After washing <sup>b</sup>	
Polytetra fluoroethylene (Teflon)	2210	20	18	—	no
Polyethylene (low density)	1550	20	20	—	no
Polyethylene (high density)	1560	20	21		no
Polypropylene	2750	21	23	18	yes
Polystyrene	2540	16	22	16	yes
Poly(methyl methacrylate)	2930	17	22	16	yes
Poly(hexamethylene capramide) (nylon)	2930	18	20	19	no
Poly(ethylene terephthalate)	2360	19	20	—	no
Stainless steel	2560	20	19	—	no

<sup>a</sup> Contact time, 5 min.

<sup>b</sup> Washed using *n*-hexane after peeling. The change in radioactivities of adhesive surfaces is due to the difference in thickness of the adhesive layer.

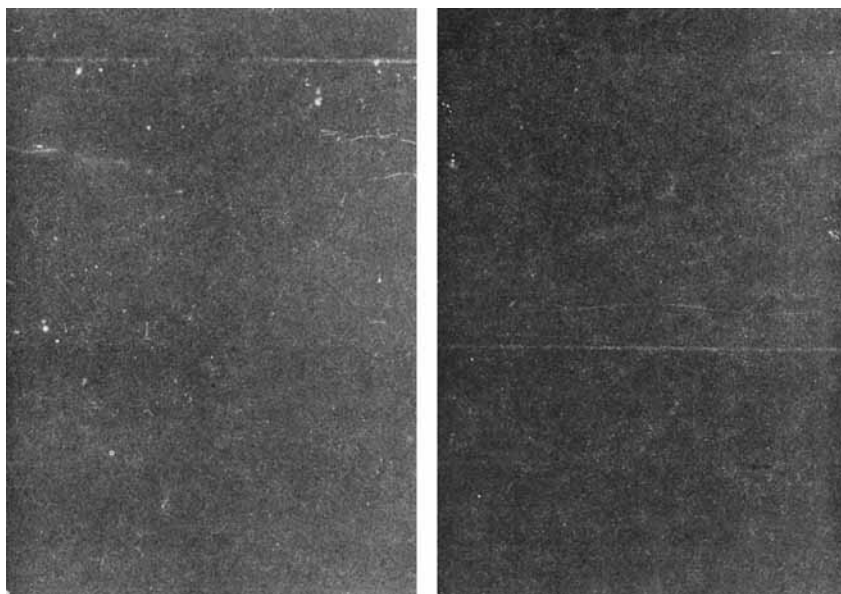


Fig. 4. Radioautographs for plastic plates after peeling: (A) polystyrene plate; (B) high-density polyethylene plate; adhesive, natural rubber/labeled hydrogenated rosin ester; exposure time, 50 days.

TABLE II  
Changes in Radioactivity Before and After Application of Labeled  
Adhesive Composed of Acrylic Copolymer<sup>a</sup>

Substrates	Radioactivity, cpm				Contami- nation
	Surface of adhesive	Before appli- cation	After peeling	After washing <sup>b</sup>	
Polytetra- fluoroethylene (Teflon)	5320	19	20	—	no
Polyethylene (low density)	4280	20	21	—	no
Polyethylene (high density)	5080	20	20	—	no
Polypropylene	5510	21	20	—	no
Polystyrene	7170	17	34 <sup>c</sup>	18	yes
Poly(methyl methacrylate)	5910	19	24 <sup>c</sup>	19	yes
Poly(hexamethylene capramide) (nylon)	5630	18	19	—	no
Poly(ethylene terephthalate)	5090	18	19	—	no
Stainless steel	5260	20	19	—	no

<sup>a</sup> Contact time, 5 min.

<sup>b</sup> Washed using *n*-hexane after peeling.

<sup>c</sup> Peeled slowly towards vertical angle direction to avoid obvious contamination.

In Figure 4, radioautographs are shown which indicate obvious presence of radioactive fragments on the plates although there is no visible pick-off.

### Contact Angle

Table IV shows the changes in contact angle of pure water on the surface of a few plastic probes before and after contact. In the cases of polystyrene and poly(methyl methacrylate), contact angles became much lower with the number of measurement and, contrariwise, the tack values were increased. This indicates that the contamination increases with the number of contacts with the adhesive.

On the other hand, in polyethylene, the tack values decreased with the number of measurements, and changes in contact angle were not so significant. This indicates that the contamination does not increase with the number of contacts in the case of materials with low surface energy such as polyethylene.

### CONCLUSION

Pick-off was detected directly using tracer techniques and indirectly from the change in contact angle of pure water. From these results, the following conclusion can be derived:

TABLE III  
Changes in Radioactivity Before and After Application of Labeled  
Adhesive Composed of Acrylic Copolymer<sup>a</sup>

Substrates	Radioactivity, cpm				Contami- nation
	Surface of adhesive	Before applica- tion	After peeling	After washing	
Polytetra- fluoroethylene (Teflon)	3730	19	17		no
Polyethylene (low density)	3880	20	31	19	yes
Polyethylene (high density)	3550	20	26	22	yes
Polypropylene	4850	20	30	20	yes
Polystyrene	5150	20	25 <sup>b</sup>	17	yes
Polystyrene	5050	19	(3932)	22	yes
Poly(methyl methacrylate)	4780	20	24 <sup>b</sup>	19	yes
Poly(methyl methacrylate)	4990	19	(3980)	19	yes
Poly(hexamethylene capramide) (nylon)	4820	19	17		no
Poly(ethylene terephthalate)	4990	19	24	20	yes
Stainless steel	4940	19	17		no

<sup>a</sup> Contact time, 20 hr.

<sup>b</sup> Peeled rapidly toward vertical direction to avoid the residue of obvious pick-off.  
Values in parenthesis show the results obtained in the presence of visible pick-off.

TABLE IV  
Changes in Contact Angle of Pure Water on the Surface of Plastic Probes  
Before and After Measurement of Butt Tensile Tack for Adhesive  
Composed of Natural Rubber and Hydrogenated Rosin Ester<sup>a</sup>

Substrate	Number of contacts	Contact angle, degrees	Av. tack value, g/cm <sup>2</sup>
Polystyrene	0	95	—
	1	95	1420
	10	82	1420
	20	46	3980
Poly(methyl methacrylate)	0	95	—
	1	71	2520
	10	61	2660
	20	67	2300
Polyethylene (high pressure)	0	95	—
	1	94	1020
	10	80	510
	20	100	560
(Surface of adhesive)		68	

<sup>a</sup> At 45% R.H., 20°C. Contact time, 1 sec; rate of separation, 1 cm/sec; contact pressure, 100 g/cm<sup>2</sup>.



The adhesive bond breaking will be truly intersurface failure in the case of materials with very low surface energy such as Teflon; however, in many materials with considerably high surface energy, the bond breaks by cohesive failure although unbonding was apparently observed as intersurface failure. Therefore, the mechanism for the unbonding process proposed in our preceding paper<sup>1</sup> has been supported.

Pick-off has also been detected from the infrared spectra of extracted residue from glass plates with a total area of 0.647 m<sup>2</sup> after peeling the adhesive tape composed of natural rubber and polyterpentine resin.<sup>6</sup> Hock<sup>2</sup> has also indicated that the surface of stainless steel probes was changed before and after measurement of butt tensile tack using electron microscopy.

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