

Studies on Adhesion of Allylic Resin. I. Adhesion of Diallylphthalate Resin and Dichromate-Treated Copper Foil

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Synopsis

An effective copper surface treatment for adhesive bonding of copper foil and diallylphthalate resin was investigated.

It involves dipping the copper foil in the potassium dichromate-sulfuric acid solution ($K_2Cr_2O_7$:76 g/l, H_2SO_4 :0.67 N) at 60°C for 5 min. The dichromate treated copper foil and glass based prepregs of diallylphthalate resin were laminated under the pressure of 38 kg/cm² for 30 min at 145°C.

Interface characteristics of the dichromate treated copper foil and diallylphthalate resin were examined.

It was found that chromium is formed on the surfaces of the treated copper foil, and allyl groups in diallylphthalate molecule are oriented to the atoms, that is, the adhesive bonding is performed by the chemical affinity of chromium and allyl groups.

The allyl group has a delocalized π -electron system, and that its bonding to a transition metal as chromium is appropriate and justifiable by quantum chemical considerations.

INTRODUCTION

Allylic resins have excellent characteristics of dimensional stability and electrical resistance, so that their application to devices of electrical communication is expected.

In spite of this aspect, allylic resin has little affinity with metallic, glassy, and cellulosic materials which are usually used for the bases of the composite materials.

The authors, recently, carried out the graft copolymerization of MMA and butadiene in order to improve the affinity of cellulose with allylic resin.^{1,2} It was our next purpose to enhance the affinity of metallic material to the resin and it can be considered, in this report, that the affinity is measured by the adhesive strength of allylic resin and copper foil.

In order to improve the adhesive strength of allylic resin and copper foil, the chemical surface treatments of copper foil surface were investigated and the dominant factors which are contributing to the adhesion were studied.

For the chemical surface treatment of copper foil, the treatments with potassium dichromate-sulfuric acid solution were carried out. The surface characteristics of the treated copper foil and allylic resin contacted with the adherend were investigated.

EXPERIMENTAL

The electrolyzed copper foil (70 μ -thickness) was used and it was defatted with trichloroethylene before the surface treatment.

As for the allylic resin, the glass based prepreg of diallylphthalate (DAP) resin was employed.

Chemical surface treatment of copper foil was accomplished as follows: the copper foil was dipped in potassium dichromate-sulfuric acid solution at 60°C for 5 min, the treated copper foil was washed in flowing water and dried in an oven at 100°C for 10 min. The treated copper foil was stored over phosphorus pentoxide (P_2O_5) in a desiccator until the adhesive experiments.

Adhesive bonding was performed under pressure and heating, that is, the copper clad laminates of DAP were prepared under a pressure of 38 kg/cm² for 30 min at 145°C.

Adhesive strength of DAP to the treated copper foil was determined by measuring the peel strength (180°) to the adherend. The peeling test was carried out in the conditioning room at 20°C, 65% R.H., and peel rate was 100 mm/min.

Characteristics of the Dichromate Treated Copper Foil and Adhesive Strength

Effect of the concentration of sulfuric acid in dichromate solution on the peel strength was tabulated in Table I, and surface characteristics of the treated copper foil specimens were collected in Table II.

TABLE I
Effect of Peel Strength of Concentration of Sulfuric Acid
in Dichromate Acid Solution

Specimens no.	Contents of treating solution			Treating conditions		Peel strength, kg/cm
	Water	K ₂ Cr ₂ O ₇	H ₂ SO ₄	Temp.	Time	
1			Nontreatment			0.00
2	11	76 g	5 ml	60°C	5 min	0.67
3	11	76 g	10 ml	60°C	5 min	0.96
4	11	76 g	18 ml	60°C	5 min	1.22
5	11	76 g	25 ml	60°C	5 min	1.03
6	11	76 g	50 ml	60°C	5 min	0.68

TABLE II
Characteristics of the Surfaces of Dichromate Treated Copper Foil

Specimens no.	Roughness factor	Contact angle of DAP monomer solution, deg.	Number of adsorbed DAP molecules, 100 \AA^{-2}	Observation by electron microscope	X-ray intensity of Cu_2O	Fluorescent X-ray intensity of $\text{CrK}\alpha$
1	1.0	28.0	24	Flat	— ^a	— ^a
2	2.2	19.0	—	Low rough	+	+
3	2.8	19.5	58	Middle rough	+	+++
4	3.5	19.0	52	High rough	++	+++
5	5.2	20.5	—	Very high rough	+++	++
6	6.8	20.0	31	Very high rough	+++	+

^a —: not obs.; +: weak; ++: strong; +++: very strong.

Surface Roughness

As evidenced from Table II, the roughness factor of the treated copper foil surface was increasing with increase of the concentration of sulfuric acid in the dichromate solution, but a correlation was not observed between the roughness factor and adhesive strength.

Contact Angle of DAP Monomer

It is important to elucidate the wettability between the treated copper foil and DAP in order to discuss the adhesion phenomena. The contact angle of DAP monomer on the dichromate treated copper foil was measured at room temperature. These results are shown in Table II.

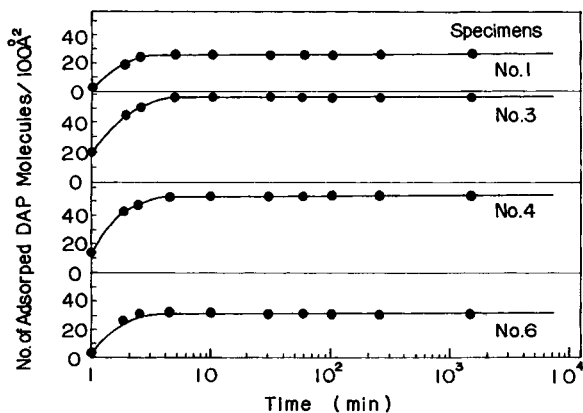
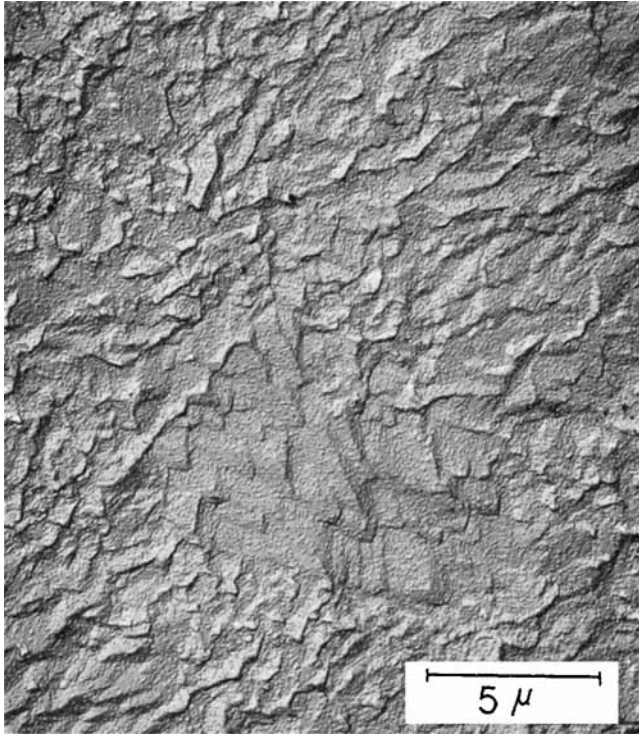
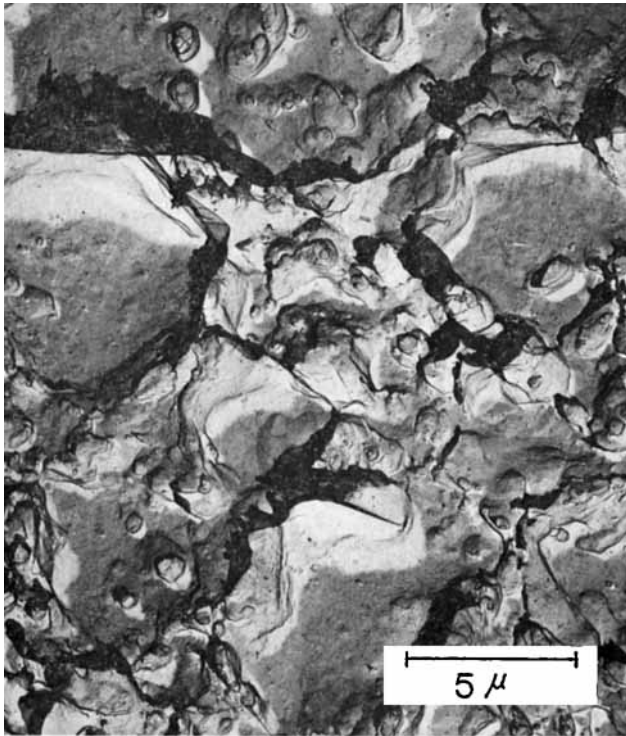


Fig. 1. Chemical adsorption of DAP monomer toward the dichromate treated copper foil surfaces in acetone dilute solution at room temperature.

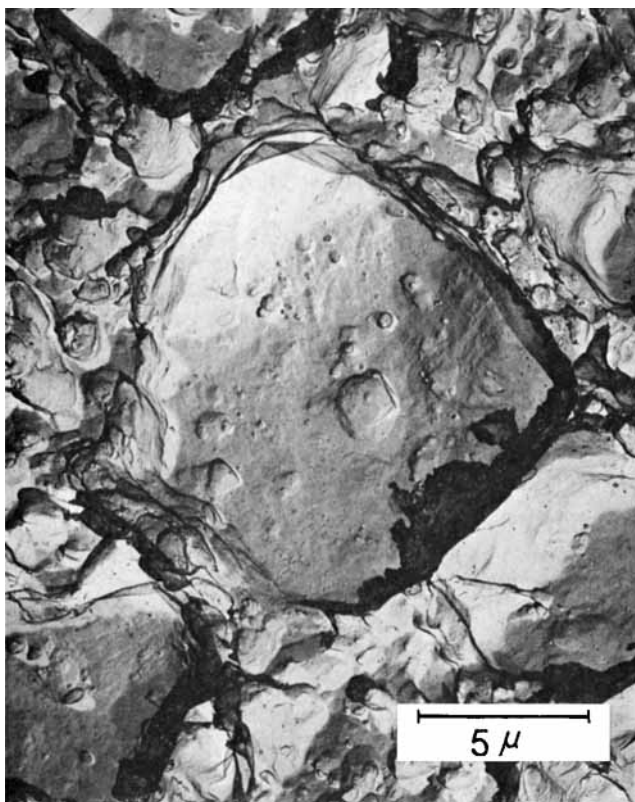


(a)



(b)

Fig. 2 (continued)



(c)

Fig. 2. Dichromate treated copper surfaces by electron microscopy (a) No. 1; (b) No. 4; and (c) No. 6 in Table I ($\times 6000$).

It showed that the contact angle on nontreated copper foil was 28° and contact angle on the dichromate treated specimens were 19° – 20° . However it cannot be ascertained from these data that the treated specimens are more wettable than the nontreated copper foils, since it is well known that the apparent contact angle decreases with increasing surface roughness.³ It suggests, although, that the increase of the surface roughness is effective for the adhesive bonding.

Chemical Adsorption of DAP Monomer

DAP molecule was adsorbed on the treated copper surface from the acetone dilute solution (8.44×10^{-4} mole/l) at room temperature. The adsorption curves are shown in Figure 1 and the number of adsorbed molecules in equilibrium are tabulated in Table II by considering the roughness factor of substrate surfaces.

The obtained adsorption isotherms (Fig. 1) can be interpreted in the manner of chemical adsorption⁴ that is corresponding to the monolayer ad-

sorption of DAP. The molecules were adsorbed in large excess, even if the roughness factors of specimens are considered. It may be considered the dichromate treated surfaces have many micropores, which will not be detected by the surface roughness measurement. Furthermore, the micropores are closely related to the adhesive bonding since the relationships of peel strength and the number of adsorbed DAP molecules are quite obvious.

Surface Observation by Electron Microscope

Figure 2 (a), (b), and (c), as example, represent the surfaces of specimens No. 1, No. 4, and No. 6 in Table I, respectively.

The results of the observation, as was expected, were similar to that of the surface roughness measurement and we were incapable of observing the micropore.

X-ray Analysis

The x-ray diffraction peaks of the treated copper foil surfaces were measured by an automatic recording diffractometer with $\text{CuK}\alpha$ radiation in the angular range of $2\theta = 20^\circ\text{--}80^\circ$. New peaks corresponding to Cu_2O were observed in the treated copper surfaces.

As shown in Table II, qualitatively, the peak strength of Cu_2O increases with the concentration of sulfuric acid in the treating solution, but no relationships are found between the adhesive strength and Cu_2O peak height.

Fluorescent X-ray Analysis

Fluorescent x-ray diffraction spectra of the dichromate treated copper surfaces are shown in Figure 3, and qualitative values of diffraction strength of $\text{CrK}\alpha$ were tabulated in Table II.

These results support the postulation of linear relationships of the adhesive strength and the quantity of chromium on the surface.

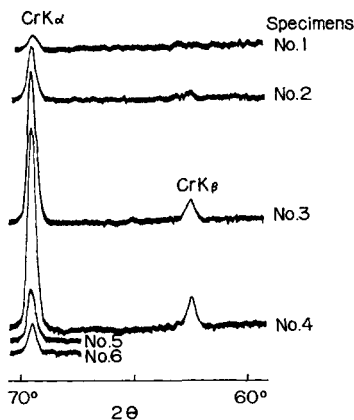


Fig. 3. Fluorescent x-ray reflection spectra of the dichromate treated copper-foil surfaces.

From the above results, it may be concluded that chromium on the dichromate treated copper foil is the dominant factor in the adhesive bonding with DAP, in addition, the surface roughness and Cu_2O formation are secondary factors involved with the adhesive strength.

Interfacial Investigation of Molecular Orientation of Diallylphthalate Resin

Figure 4 shows a schematic diagram of the laminates of copper foil and DAP resin. Peel strength is attained to 1.2 kg/cm at the surface *A* and is not given at the surface *B*. The investigations of the surface characteristics of the *A* were developed in order to obtain the information on the causes of the adhesive strength. No residual inorganic materials were detected on the surfaces of DAP resin which was examined by using x-ray fluorescent technique.

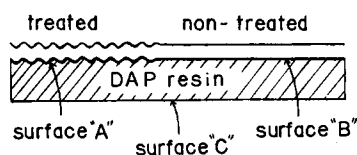


Fig. 4. Schematic diagram of surfaces of cured DAP resin.

Contact Angle of Water

Table III shows the contact angle of water (20°C) on the surfaces *A*, *B*, and *C*. The surface *A* is hydrophobic. After the sand blasting of the surface *B*, the contact angle was 23.6° . This means that the roughing up of the surface contributes to decrease the value of contact angle. The hydrophobic property of the surface *A* is out of relation to the surface roughness.

Heat treatments of the surface *A* and *B* were made in vacuo at 150°C . The effect of the duration times on the contact angle is shown in Figure 5. Highly interesting results were obtained by these experiments. The contact angle values of the surface *A* are decreasing with increasing of heat-

TABLE III
Surface Density and Contact Angle of Water (20°C) on the Surfaces *A*, *B*, and *C*

Experiments	Surfaces		
	<i>A</i>	<i>B</i>	<i>C</i>
Surface density (g/cm^3)	1.306	1.245	—
Contact angle of water (20°C) on the surfaces (degree)	86.0	24.5	23.5
Contact angle of water (20°C) on the surfaces treated in vacuo at 150°C for 22 hr (degree)	25.0	24.0	23.0

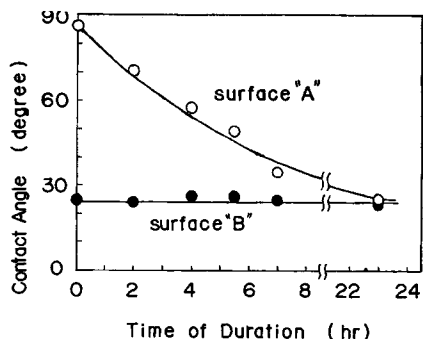


Fig. 5. Change of the contact angle of water on the surfaces *A* and *B* by the heat treatments of the surfaces in vacuo at 150°C.

ing duration time, while the values of the surface *B* are not changed by the heat treatments.

Surface Density and Molecular Orientation

The density of the regions of the surface *A* and *B* were measured in a density-gradient column of carbon tetrachloride—ethyl alcohol mixture solution at room temperature. These results are shown in Table III. J. P. Luongo and H. Schonhorn,⁵ recently, have found the substrate effect on the surface density of polyethylene. Also, in this study, the difference of the density of the surfaces *A* and *B* corresponds to that of the surface energy of the substrate, nontreated copper foil and the dichromate treated specimens.

Since the density is associated with crystallinity, DAP molecules are supposed to be preferentially oriented in the region of the surface *A*, and, on the other hand, randomly distributed in the region of *B*. By the heat treat-

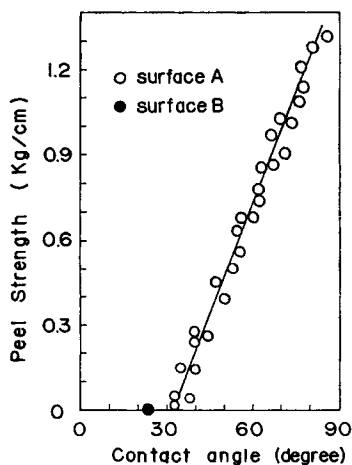


Fig. 6. Interrelation of peel strength and the contact angle of water on the surface *A*.

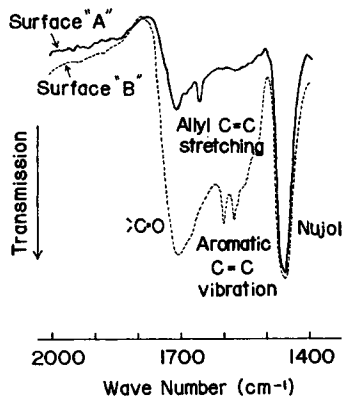


Fig. 7. ATR spectra of the surfaces *A* and *B* of DAP resin.

ments of the surface *A*, the orientation of the molecules ought to be gradually dispersed to result in an increase of wettability (Fig. 5).

The present consideration is further illustrated by the following experiments, in which the relation of adhesive strength and contact angle of water (20°C) on the surface *A* was determined. Evidently from Figure 6, linear relationship is observed between the adhesive strength and the contact angle of water which is a parallel relation to the degree of the molecular orientation in the region of the surface *A*.

On the other hand, it is believed that the surface *A* has low surface energy since the surface is less wettable, that is, low cohesive energy groups in DAP molecule are oriented to the surface *A*. Cohesive energy of the groups in DAP are listed,⁶

=CH_2	1780 cal/mole
=CH—	990 cal/mole
=CO	4270 cal/mole

From the arguments, one may be able to believe that the allyl groups in DAP molecule are oriented to the surface *A*.

Furthermore, the surface region of the resin was examined by using attenuated total reflection (ATR) technique (KRS-5 crystal) and the spectra of the surface *A* and *B* are shown in Figure 7. The spectra were recorded using nujol coated samples in order to avoid the light scattering of the infrared ray due to the surface roughness.

In Figure 7, the ATR spectra are shown at 1730 cm^{-1} of >C=O as it appears in both specimens of the surface *A* and *B*. The 1645 cm^{-1} component of the surface *A* is associated with the allyl group C=C stretching mode, and the 1598 cm^{-1} component of the surface *B* is aromatic C=C vibration. That is to say, the allyl component appears in the surface *A* but not in the *B*, and the aromatic component appears in the surface *B* but not in the *A*.

From the above mentioned analysis, it may be able to consider that the allyl groups are oriented to the surface *A* region.

Adhesion under the Applied Electric Field

The allyl group compelled to orient toward the surface *A* region by polarization of DAP molecule under the applied static voltage. The laminating technique is shown in Figure 8.

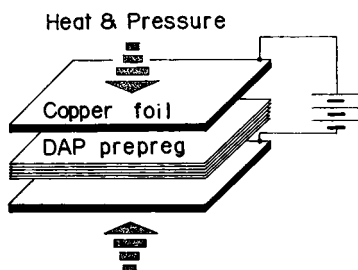


Fig. 8. Laminating technique of the treated copper foil and DAP prepreg under the applied static voltage.

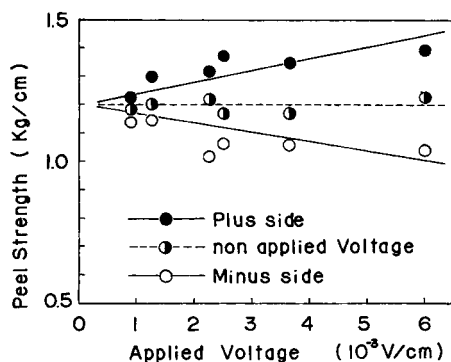


Fig. 9. Effect of the applied static voltage on the peel strength.

The effect of the applied voltage on the peel strength is illustrated in Figure 9. Peel strength of the plus side is stronger than the minus side and the differences of the peel strength of both sides are increased with increase of the applied voltage.

This indicates that the electron negative group of allylic is oriented by the electric field to the electron positive plus side. It may be concluded that the peel strength, which results from the oriented allyl group, was strengthened at the interface of the plus side.

From the preceding discussions, it is believed that the predominant factor of the adhesive bonding of the dichromate treated copper foil and DAP resin is the chemical affinity of chromium to the allyl group in each adherend and adhesive, respectively.

The theoretical aspects were investigated to understand the mechanism of the chemical affinity of chromium and allyl group.

Allyl π -Complex of Chromium

The authors estimated the degree of covalent bonding between the allyl group and chromium and copper in order to infer the chemical affinity of the group to the transition metals.

The allyl group has C_{2v} symmetry and it belongs to the irreducible representation of $A_1 + 2B_1$. By the LCAO-MO calculation, we obtain the molecular orbitals of $p\pi$ orbital in allyl group.

$$\psi_{B_1} = \frac{1}{2} (\phi_1 + \sqrt{2} \phi_2 + \phi_3)$$

$$\psi_{A_2} = \frac{1}{\sqrt{2}} (\phi_1 - \phi_3)$$

$$\psi_{B_1'} = \frac{1}{2} (\phi_1 - \sqrt{2} \phi_2 + \phi_3)$$

From the group theory, the orbitals of the metals, coordinating to the ligand, are determined as follows,

$$\begin{array}{ll} \psi_{B_1} & d_z, s, p_z \text{ } (\sigma\text{-bond}) \\ \psi_{A_2} & d_{xy}, p_x \text{ } (\pi\text{-bond}) \\ \psi_{B_1'} & d_{yz}, p_y \text{ } (\pi\text{-bond}) \end{array}$$

the other orbitals, $d_{x^2-y^2}$, d_{xy} , are of the nonbonding type. Accordingly, the allyl group is capable overlapping with the transition metals through one σ - and two π -bondings. The allyl group, on the basis of the foregoing arguments, may be capable chelate formation with the transition metal.

In order to estimate the strength of the bond of the ligand, overlap integrals were calculated by using the Slater's rules and Richardson's function,⁷ for $2p\pi$ orbital of allyl group and $3d$ radial function of transition metal, respectively.

For example, the overlap integrals (S) of Cu^{++} and Cr^{++} with the allyl group are as follows,

$$\begin{array}{ll} Cu^{++} & \text{Allyl group; } S = 0.113 \\ Cr^{++} & \text{Allyl group; } S = 0.198 \end{array}$$

From the above mentioned calculation, it is known that the covalency of Cr^{++} with the allyl group is strong, on the other hand, Cu^{++} is weak. That is, the molecule with an allyl group tends to produce the coordination compound with chromium in comparison with copper.

It may be concluded, on the basis of the foregoing discussions, that the chemical affinity of the allyl group with chromium is the dominant causes of the adhesive strength of DAP resin and the dichromate treated copper foil.

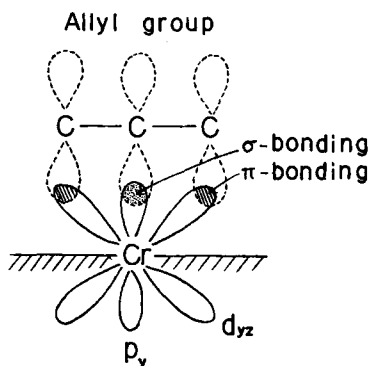


Fig. 10. Model chelate compound of chromium and allyl group on the dichromate treated copper surface.

Figure 10 illustrates the coordinate bonding of the allyl group and chromium.

We wish to acknowledge helpful discussions made in connection with this work by Dr. M. Katagiri, Dr. K. Matsumae, Dr. K. Iino, Dr. H. Toyota, and Dr. K. Nakagawa of our laboratory.

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Received April 11, 1969

Revised June 3, 1969