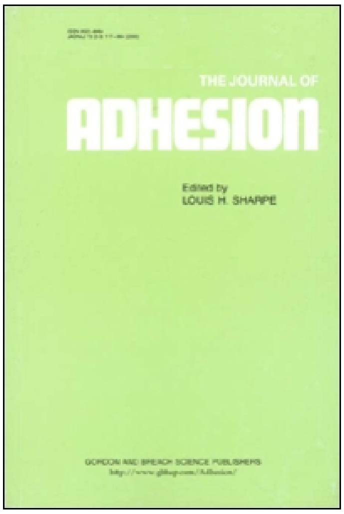

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Simulation Analyses on the Diffusion of a Rust-Preventing Oil into an Oil-Accommodating Adhesive

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In recent years bonding between two steel plates was accomplished with an oil-accommodating adhesive without requiring degreasing of the steel. In this paper, the exclusion process of the oil was investigated in this adhesive on the assumption that the oil was absorbed into the adhesive layer.

It was found that the oil layer essentially disappeared in the initial step of curing in which the temperature was raised to 180° C, because the diffusion rate of the oil into the adhesive increased abruptly with temperature. Therefore, the bonding process in this case is not influenced by the presence of oil on the steel plates.

KEY WORDS: oil-accommodating adhesive; rust preventing oil; diffusion of oil; simulation; steel plate; adhesive bonding; contamination

INTRODUCTION

Many methods can be considered for joining steel plates, *e.g.*, riveting, welding, adhesive bonding, etc. The use of adhesive bonding has increased significantly in industry. However, the surface of steel plates is covered by a layer of oil for conservation and protection from rusting. Because oil is a hindrance to adhesion, the surface of steel plates is generally degreased before adhesive bonding.

If it were to be possible to attain adhesive bonding without degreasing, the use of adhesives would be promoted. An oil-accommodating adhesive was developed in the 1970's[1–3] for such demands, and bonding between steel plates was attained with this adhesive without degreasing. The absorption of oil into adhesive may be a very important factor because it has been believed that the bonding between oily steel plates occurs after the oil is removed from the surface of the plates.

Graham,[4] Debski[5,6] and Nakajima[7] have suggested the following two kinds of processes for bondng with an oil-accomodating adhesive. The first process is the replacement of the oil layer by the adhesive. That is, the monomer of the adhesive reaches the surface of the adherend through the oil layer and the bonding starts. The other process is the absorption of oil into the adhesive layer. In this case, the oil is removed from the surface of steel plates by absorption into the adhesive layer, and the bonding is attained. However, no paper has yet discussed concretely the diffusion of the oil into the adhesive layer. Therefore, we have tried to simulate the absorption process of oil into adhesive layer.

In this paper, we obtained the absorption of the oil into the adhesive layer by a model in which the oil diffuses from both sides of the adhesive layer, as shown in Figure 1. The diffusion coefficient of the oil into the adhesive was obtained by the determination of the oil concentration in the adhesive as a function of time. The oil distribution in the adhesive layer under some conditions was calculated numerically, and was predicted the time when the oil layer disappeared essentially completely from the surface of the steel plates. Details on this result will be described in this paper.

EXPERIMENTAL

Materials

The composition of oil-accomodating adhesive used in this study is shown in Table I. The main component of the adhesive is epoxy resin, and the adhesive was supplied by Toyoda Gosei Co., Ltd. (Nagoya, Japan). The hardener is already included in it. The adhesive composition is designed so as to finish curing at near 180° C, because the curing can be carried out together with paint-drying in vehicles. Further, it was already confirmed elsewhere[6,8,9] that this adhesive works very well as an oil-accommodating

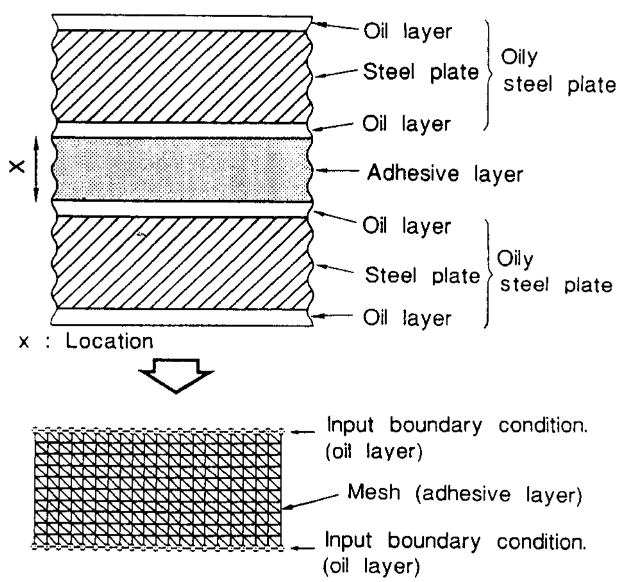

FIGURE 1 Model for simulation.

TABLE I
Components of oil-accommodating adhesive

Component	Content (wt.%)
Epoxy resin (Bisphenol A type) + Hardener (Dicyandiamide)	69.0
Filler (Sillica gel and $CaCO_3$)	27.5
Nitrile rubber (Modified)	3.5

one. We used Metal Guard 831® (Mobil Oil Co., Ltd., Tokyo, Japan) as the rust-preventing oil.

Curing of Adhesive

The adhesive used in this study is of the heat-curing type, as mentioned previously. The degree of curing of the adhesive was determined by making use of the fact that the amount of heat of reaction remaining in the adhesive decreases with the extent of cure.

The curing of the adhesive was carried out in a press (SA-302 (II), TESTA SANGYO Co., Ltd., Tokyo, Japan). The heat of reaction was determined by DSC (DSC 8230 RIGAKU CORPORATION, Tokyo, Japan), at a heating rate of 10° C/min. The extent of cure of the adhesive was obtained by comparing the heat of reaction with that of fully-cured adhesive.

Concentration of Oil in Adhesive

Oil concentration in the adhesive was determined by the method shown in Figure 2. Small rectangular holes were made on the side of the test tube for removing adhesive after a diffusion experiment. The holes were sealed with heat-resistant tape from the outside. The adhesive was introduced into the test tube and the oil was carefully placed on the adhesive. The oil diffusion experiment was carried out in a thermostatic chamber at a given temperature. The adhesive containing the oil was taken out by inserting a spatula into the test tube through the holes. The oil concentration in the adhesive was determined by the following processes.

Infrared spectra (100 were accumulated) were measured in an FT-IR instrument (FT-200, HORIBA Co., Ltd., Kyoto, Japan), and the absorption intensity at 2854 cm^{-1} due to the oil was obtained by subtracting the spectrum of the original adhesive from that of the adhesive containing the oil. The oil concentration in the adhesive was determined from the calibration curve shown in Figure 3, which was obtained in advance.

In addition, the saturation concentration of the oil in the adhesive was found to be 5.0 wt.%. This result is important for the calculation of the time when the oil disappears from the steel plate surface.

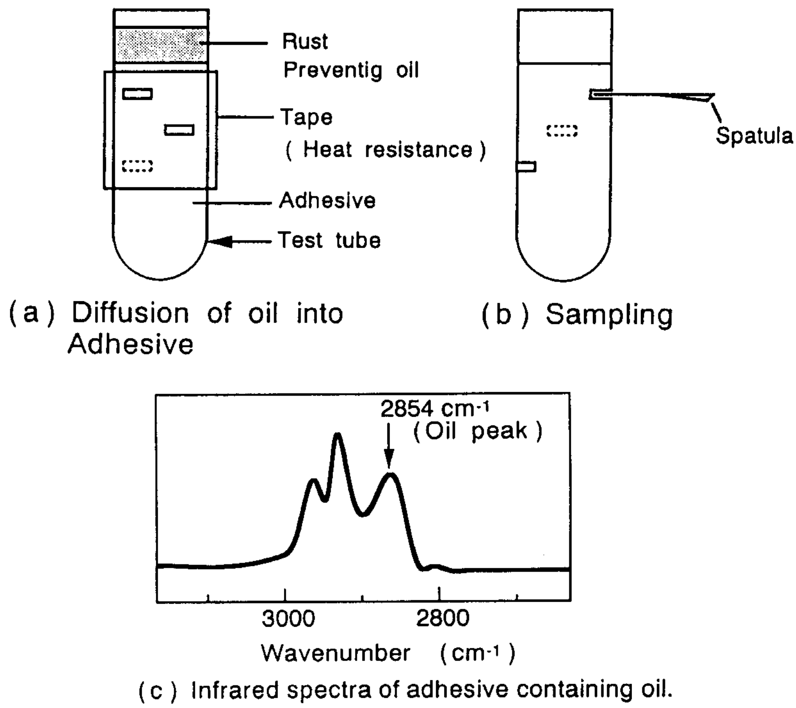

FIGURE 2 Experiment on oil diffusion into adhesive.

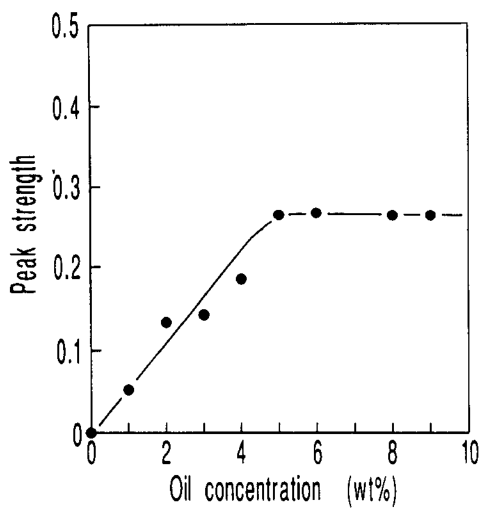

FIGURE 3 Calibration curve for determination of oil in adhesive. The peak intensity of oil was determined at 2854 cm^{-1} in IR spectrum.

CALCULATIONS

Calculation Program

The calculation on the diffusion of the oil was conducted by modifying the program for thermal stress analysis. "PC-9801 Finite Element Method, Programming of Thermal Stress Analysis on Non-steady State" (NIKKAN KOUGYOU SINBUNSYA, Tokyo, Japan). Namely, the program was used after replacing heat by oil concentration, and thermal conductivity by diffusion coefficient. We call this method FEM here after. The diffusion equation of the oil into the adhesive can be expressed by Equation (1).

In this program, the diffusion equation was solved based on the implicit finite-difference method (Crank-Nicolson method). Therefore, c in Equation (1) is a function of the independent variables x and t. The x-axis was divided into i equal divisions by steps of h and, similarly, the t-axis was divided into j equal divisions by steps of k.

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{1}$$

where c: the oil concentration (wt.%); t: diffusion time (s); D: diffusion coefficient (m^2/s); x: location from the interface between the oil and adhesive (m)

Thus, Equation (1) can be expressed by Equation (2).

$$(1+2r)c_{i+1,j} - r(c_{i+1,j+1} + c_{i+1,j-1}) = (1-2r)c_{i,j} + r(c_{i,j+1} + c_{i,j-1}) \tag{2}$$

where $r = k/h^2$, $h = c_{i,j+1} - c_{i,j}$ and $k = c_{i+1,j} - C_{i,j}$.

The three c's on the right side in Equation (2) are known, and those on the left side are unknown. This equation means that the oil concentration in a given time at a given location can be obtained from the values prior to that time and location. This principle can be explained using the x-t plane shown in Figure 4; x, as indicated above, indicates the distance from the interface between the oil and adhesive, and t means time. So the oil concentration is stored in each grid point (mark "●" in Figure 4) in simulation. As an initial condition, a given value as a boundary condition is input to the concentrations $c_{1,1}$ and $c_{1,m}$ at both end columns (mark "■" in Figure 4), and the value of 0 wt.% is input to all the other $c_{1,j}$. For example, c_{21}, c_{22} and c_{23} are unknown, and c_{11}, c_{12} and c_{13} are known. One equation is obtained using these six concentrations, though in this case c_{21} is exceptionally known. When the calculation unit is shifted to the right, the unknown quantities are c_{22}, c_{23} and c_{24} and the known quantities are c_{12}, c_{13} and c_{14}. When calculation unit is fixed at the first row, the column is shifted horizontally from the second column to (m − 1)th column, and the first order simultaneous equations composed of (m − 2)th elements is obtained. When the simultaneous equations are solved, all the oil concentration of the second row is obtained since c_{21} and c_{2m} are known in advance. Thus, the distribution of the oil concentration can be calculated in the adhesive layer by carrying out these processes continuously.

This method was applied for the determination of diffusion coefficient from experimental data and for simulation to the process of oil into adhesive.

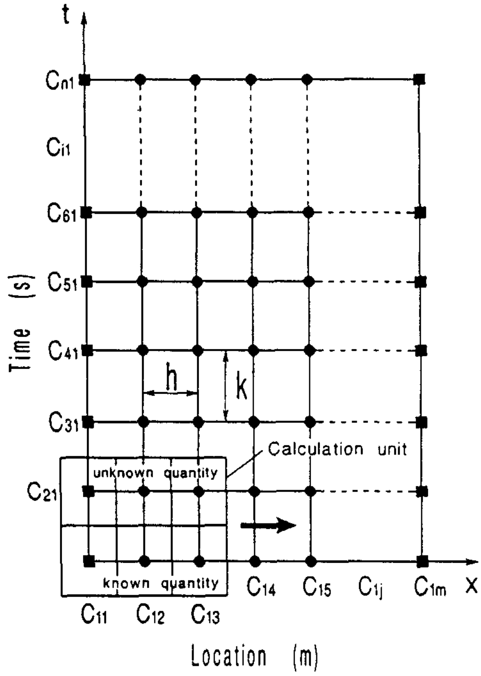

FIGURE 4 Calculation principle for Crank-Nicolson method. ■: Grid to input boundary condition.

Calculation of Diffusion Coefficient

The oil concentration c is expressed as a function of x, t and D, as shown in Equation (3). In general, for a given x and t, the oil concentration c can be determined experimentally, but the diffusion coefficient D is unknown. For fixed x_{exp}, t_{exp}, and an arbitrarily chosen D_i, a calculated concentration c_{cal} is obtained using Equation (2) as shown in Equation (4). This method was applied for the determination of the diffusion coefficient from experimental data and for simulation of the process of oil diffusing into adhesive. Further, the oil concentration c_{exp} can be obtained experimentally for fixed x_{exp} and t_{exp}. The difference, Δc, between the c_{exp}, and the c_{cal} is calculated according to Equation (5). This calculation is conducted for several c_{exp}, x_{exp} and t_{exp}. The diffusion coefficient D was determined so as to minimize S in Equation (6).

$$c = f(D, x, t) \tag{3}$$

$$c_{cal} = f(D_i, x_{exp}, t_{exp}) \tag{4}$$

$$\Delta c = (c_{exp} - c_{cal})^2 \tag{5}$$

$$S = \sum \Delta c \tag{6}$$

A diffusion coefficient is generally expressed as a function of temperature.

$$D = D_0 \exp(-E/RT) \tag{7}$$

where D: diffusion coefficient (m^2/s); D_0: constant (m^2/s); E: activation energy of diffusion (J/mol); R: gas constant (J/mol.K); T: temperature (K).

When we plot log D against the reciprocal of T, a linear relation is generally obtained experimentally. Thus, a diffusion coefficient at any temperature can be given using this relation.

RESULTS AND DISCUSSION

Diffusion Coefficient of Oil into Adhesive

The measurement of diffusion coefficient over a wide range of temperature was actually impossible. This is because at high temperatures the curing of the adhesive occurs very fast. Therefore, in these cases, we can not determine the diffusion coefficient. On the other hand, at low temperatures we had to spend more than one year to obtain one experimental point. Further, it was very difficult to obtain the oil concentration in the adhesive near the interface between oil and adhesive according to the method shown in Figure 2. Some experimental points were finally obtained at several temperatures after many trials. The results are shown in Figure 5. The diffusion coefficients were calculated according to Equation (3)–(5), by which we can obtain an optimum value for each temperature. The temperature dependence of the diffusion coefficient is shown in

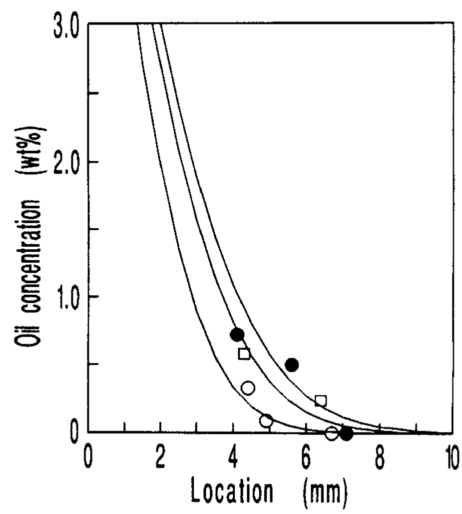

FIGURE 5 Result of diffusion of oil into adhesive. Experimental values ○:49.0° C, 120 hrs □:42.0° C, 336 hrs ●: 60.1° C, 72 hrs —: Fitted by use of Equations (3)–(5). For above experimental points, diffusion coefficients of 4.8×10^{-12} m^2/s, 2.9×10^{-12} m^2/s, and $1/.7 \times 10^{-12}$ m^2/s were obtained, respectively.

Figure 6. By assumption of Equation (7) for the relationship between temperature and diffusion coefficient, the relation can be expressed as Equation (8). From this equation, we can estimate the diffusion coefficient for any given temperature.

$$D = 2.04 \times 10^5 \times \exp\left(\frac{-1.22 \times 10^4}{T}\right) \quad (8)$$

Distribution of Oil in Adhesive Layer

We calculated the distribution of the oil in adhesive layer at 25° C by the Finite Element Method, already described. The simulation conditions were as follows; the thickness of the adhesive layer was 150 μm, that of the oil layer 3.0 μm and the diffusion coefficient 4.10×10^{-13} m^2/s, which was obtained from Figure 6. The oil concentration at both sides of the adhesive layer was 5 wt.%, which was determined from the results of Figure 3.

The time dependence of the oil concentration as a function of the location in the adhesive layer is shown in Figure 7. The time dependence at the ends of the adhesive layer is shown in Figure 8. These figures indicate that all the oil on the steel plates has been essentially completely absorbed into the adhesive layer in approximately 45.5 min, and that the concentration of the oil becomes constant everywhere in the adhesive layer in around 170 min.

Next we calculated the time at which the oil layer disappears from the steel surface in the process of heating the adhesive. Figure 9 shows the curves of temperature versus time in this simulation. Actually, these curves were obtained experimentally, supposing

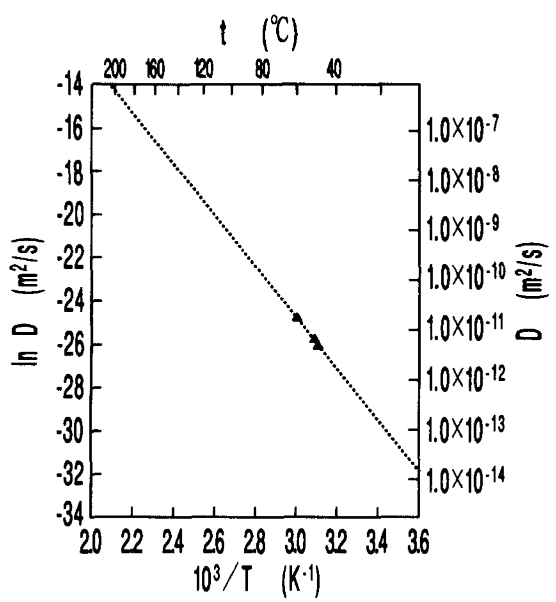

FIGURE 6 Temperature dependence of diffusion coefficient. The dotted line is a plot of Equation (8).

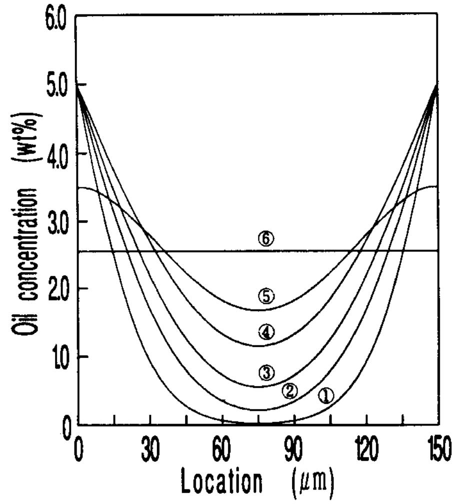

FIGURE 7 Oil distribution in adhesive layer. Time; ① 0min, ②:20 min, ③:30 min, ④:45.5 min, ⑤:60 min, ⑥:170 min. Temperature:25° C Thickness of oil layer:3.0 μm
Thickness of adhesive layer:150 μm Saturation concentration:5.0 wt.%

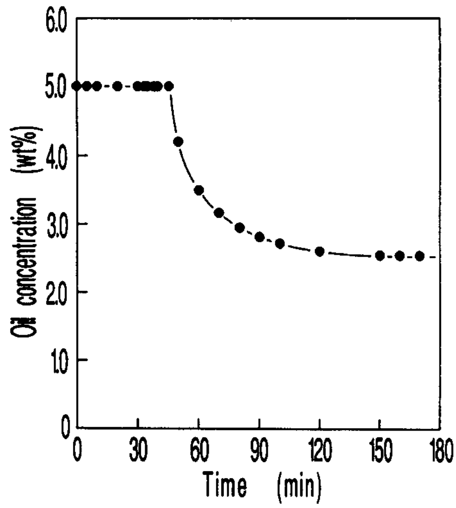

FIGURE 8 Time dependence of oil concentration in adhesive layer at adhesive surface.
Temperature:25° C Thickness of oil layer: 3.0 μm Thickness of adhesive layer: 150 μm Saturation concentration:5.0 wt.%

that the adhesive was introduced into the test press (SA-302 (II), TESTA SANGYO Co., Ltd., Tokyo, Japan), which had been heated in advance to given temperatures. The simulation conditions were the same as those at 25° C except for the temperature effect on the diffusion coefficient. The diffusion coefficient was obtained for each second from

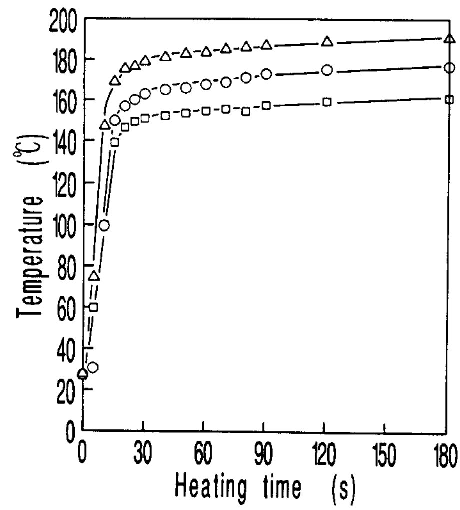

FIGURE 9 Time dependences of temperature in test press apparatus. Maximum temperature; □:160°C, ○:180°C, △:200°C

Figure 9 and Equation (8). The distribution of the oil in the adhesive layer was then calculated, based on the diffusion coefficient thus obtained. The time dependence of the oil concentration at both ends of the adhesive layer is shown in Figure 10 (elevated temperatures) which has the same meaning as in Figure 8 (25°C). When the final temperature of the adhesive is 160°C, it takes only about 11s for the oil layer to disappear from the steel plate. Essentially the same results were obtained for the other final temperatures.

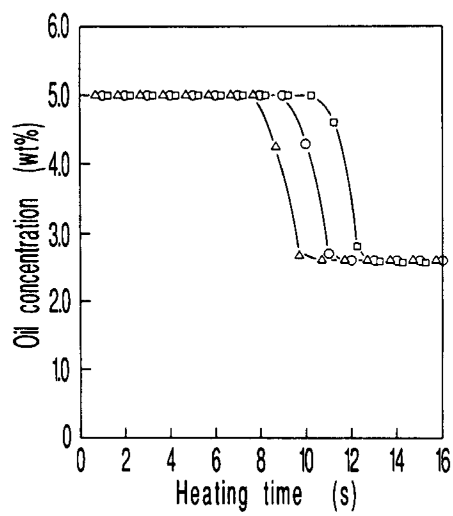

FIGURE 10 Relationship between heating time and oil concentration at adhesive surface. Maximum temperature: □:160°C, ○:180°C, △:200°C Thickness of oil layer: 3.0 μm Thickness of adhesive layer: 150 μm Saturation concentration: 5.0 wt.%

In the above calculation, the oil diffusion into the adhesive layer was calculated on the assumption that the adhesive did not cure at all. However, curing of the adhesive occurs as the time (and, thus, the temperature) increases as shown in Figure 11, the curing *rate* of the adhesive also increases with temperature. So the influence of curing on the diffusion coefficient may become important, especially for the case of 200°C. We considered the effect of curing of adhesive by correction factor α as shown in Equation (9). It was assumed that the oil did not diffuse into the cured part, but only into the non-cured part of the adhesive. In addition, it was confirmed experimentally that only a small amount of oil diffused into the cured adhesive. Therefore, the above assumption was thought to be reasonable.

$$\alpha = \frac{100(\%) - R_{cure}(\%)}{100(\%)} \tag{9}$$

where α: correction factor, R_{cure}: the degree of curing of the adhesive

The time dependence of the oil concentration on the surface of the adhesive layer is shown in Figure 12. The oil-disappearing time is seen to be only one second longer than in the case for which the curing effect was ignored. This result is due to the fact that the diffusion coefficient increases very rapidly with temperature rather than with the degree of cure of the adhesive.

In addition, in this case, the saturated concentration of oil at the interface of the adhesive decreased gradually with time. In the practical bonding process, we can consider that the oil on steel plates disappears very rapidly in the heat-curing process, and that the bonding of the adhesive with the steel plates is attained completely.

The effect of thickness of the oil layer on the oil-disappearing time was examined. The result is shown in Figure 13. The oil-disappearing time, T_{dis}, increased with the thickness of the oil layer. When the thickness is 5.7 µm, T_{dis} is about 14 s.

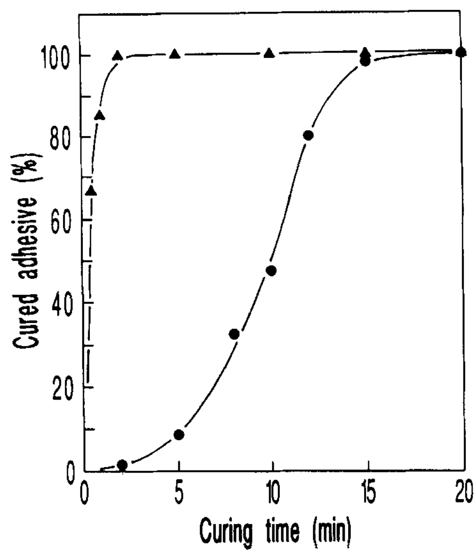

FIGURE 11 Relationship between curing time and degree of cure of adhesive. Maximum temperature; ●: 180° C, ▲: 200° C

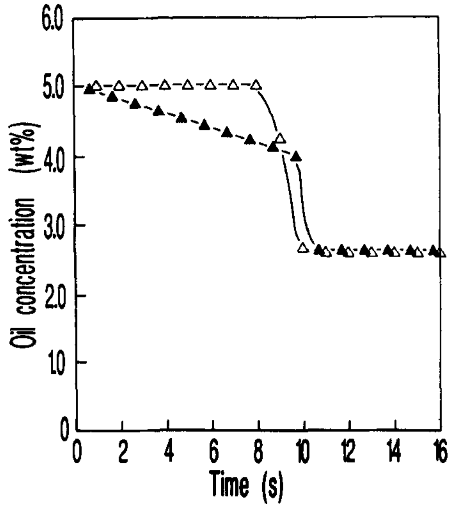

FIGURE 12 Relationship between heating time and oil concentration at interface of adhesive layer under 200°C. △:Curing effect is not considered. ▲:Curing effect is considered. Thickness of oil layer: 3.0 μm Thickness of adhesive layer: 150 μm Saturation concentration: 5.0 wt.%

When the oil layer is thicker than 5.7 μm, the oil no longer disappears from the surface of the steel plates because the amount of oil exceeds that required to achieve the maximum solubility in the adhesive.

The disappearing time, T_{dis} was calculated as a function of the thickness of adhesive layer. The result is shown in Figure 14. When the thickness of adhesive layer is 50 μm,

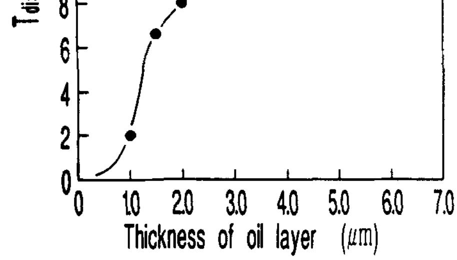

FIGURE 13 Effect of thickness of oil layer on the time when oil layer disappears by diffusion. Maximum temperature: 180°C Thickness of adhesive layer: 150 μm Saturation concentration: 5.0 wt.%

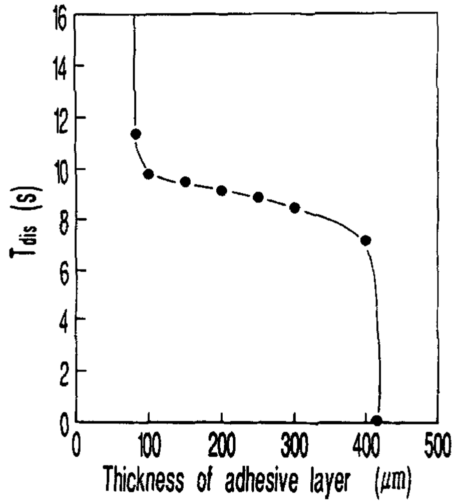

FIGURE 14 Effect of thickness of adhesive layer on the time when oil layer disappears by diffusion. Maximum temperature: 180° C Thickness of oil layer: 3.0 μm Saturation concentration: 5.0 wt.%

T_{dis} is about 6s. However, when the thickness of adhesive layer is thinner than 83 μm, the oil is always on the surface of steel plates.

The disappearing time, T_{dis}, was also calculated as a function of the saturation concentration of the oil in the adhesive layer. The result is shown in Figure 15. When the saturation concentration of the oil is less than 2.7 wt.%, the oil remains on the surface of the steel plates in the case of a 3 μm thick oil layer, which is usually observed

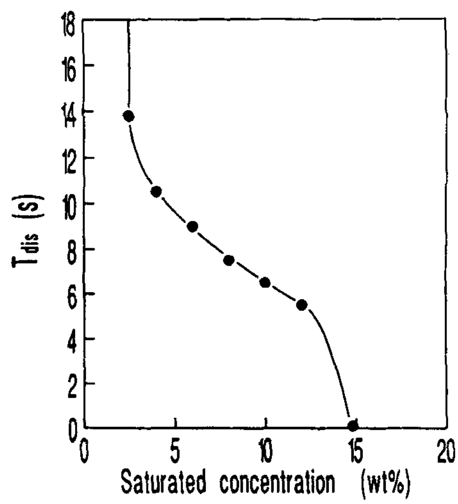

FIGURE 15 Effect of saturation concentration of oil in adhesive on the time when oil layer disappears by diffusion. Maximum temperature: 180° C Thickness of oil layer: 3.0 μm Thickness of adhesive layer: 150 μm

in practice on steel plates. Therefore, the composition or the thickness of the adhesive must be designed so as to absorb the oil completely.

CONCLUSIONS

The bonding conditions for steel plates with oil-accommodating adhesive were examined through experiment and simulation. The following conclusions were reached. It took 40–50 min for the oil to be absorbed into the adhesive layer if the bonding process was carried out at room temperature. The oil layer disappeared within 20s when the temperature of the adhesive was raised. This is due to the fact that the diffusion coefficient of the oil into the adhesive increases abruptly with temperature. When the thick, adhesive layer is very thin or the oil layer is very thick, the oil layer on the steel plates can not be absorbed into the adhesive. This occurs when the amount of oil present is sufficient to exceed its solubility in the adhesive.

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