Reaction Between Sulfur Compounds and Metal Surfaces at High Temperatures*

Toshio Sakurai**, Kachio Sato*** and Kyoza Ishida**

Summary: From the viewpoint that the action of EP additives is a kind of controlled corrosion, the high temperature corrosion of metals in hydrocarbon oils containing sulfur compounds was studied by using the Barcroft method.

The corrosion rate of iron was observed to keep the parabolic law, and the reaction between sulfur compounds and metal surfaces could conceivably be controlled by the diffusion of reactants through the formed films on the metal wire surface. With the white oil solutions of dibenzyl disulfide, the rate of corrosion process was made to deviate from the parabolic law and the intensive corrosion was observed. The action of dibenzyl disulfide apparently depends on the characteristics with which the corrosion was associated with the cracking of surface resultant layers.

It should be noted that the amount of corrosion observed in white oil alone was almost equivalent to that obtained in the case where the solution containing didodecyl disulfide or diphenyl disulfide was used. According to the data obtained by X-ray analysis of the sulfurized products, the formation of iron oxide and iron sulfide was fairly well detected. The sulfurization reaction, therefore, seems to be accompanied with oxidation reaction at high temperatures.

With the corrosion of stainless steel, the corrosion rate was observed to be very slow compared to that of iron, and in the scope of this experiment, there was no promoting action during corrosion, even when dibenzyl disulfide was used.

Introduction

It is generally recognized that the anti-wear and anti-friction properties of EP additives may be connected with their chemical reactivity toward metals, and the action of EP additives is a kind of controlled corrosion.

There have been many investigations of the action of EP additives under static conditions and dynamic conditions. We previously reported about the reaction between sulfur compounds and steel under dynamic conditions, using the tracer method¹⁾. However, little investigations has been made as to the mechanism of the reaction of EP additives with metals at high temperatures. Bowden and Tabor have shown that even in well-lubricated systems, surface temperatures in the contact region between sliding

metals could approach the melting point of the metal²⁾.

Recently Barcroft has introduced a method for studying the reaction between EP additives and metal surfaces at temperatures up to 600°C. It has been shown that the frictional behavior of sulfur compounds is different from that of other EP additives in the atmosphere without oxygen, and that the oxygen coexisting with sulfur compounds plays an important role in reducing the friction between metals³⁾. Godfrey recently has shown that there is iron oxide, for instance Fe₃O₄, on the surface films formed on steel during extreme pressure run with sulfurized mineral oils⁴⁾.

The present objective is to extend knowledge of the mechanism of the reaction between metals and hydrocarbon oils containing sulfur compounds at high temperatures. Some interesting considerations for the mechanism of corrosion are given from the experimental results.

* Received November 28, 1963.

** Tokyo Institute of Technology, 1 Ookayama, Meguro-ku, Tokyo.

*** Nippon Mining Co., Ltd., 3 Aoicho Akasaka, Minato-ku, Tokyo.

Experimental

Apparatus and Experimental Procedure

A circuit diagram of the apparatus used in this investigation is shown in Fig. 1. The apparatus essentially is the same as that shown by Barcroft.

- P₁, P₂, P₃: Potentiometer
 R₁: 10 Ω Standard resistance
 R₂: 1 Ω Standard resistance
 W: Thin metal wire
 S: Sample oil
 (M): Measuring circuit
 (H): Heating circuit

Fig. 1. Circuit diagram of apparatus used

A thin metal wire supported across two terminals was immersed in a sample oil, and the resistance of the wire was measured by the measuring circuit. Once connected to the heating circuit, the wire was heated electrically and was made to corrode. The reaction temperature was deduced from the resistance/temperature characteristics of the metal used. After the reaction, the change of the resistance was measured by the measuring circuit.

Assuming that the reaction product formed on the wire surface is non-conducting and the attack by additives is uniform over the whole of metal surface, the change in resistance may be converted to thickness of metal corroded by the following equation:

$$\Delta r \approx \left(\frac{\Delta R}{\Delta R + R_0} \right) \left(\frac{r_0}{2} \right) \quad (1)$$

where Δr = thickness of metal corroded, ΔR = change in resistance due to corrosion, R_0 = initial resistance of wire, and r_0 = radius of wire.

Since the thickness of metal corroded was easily deduced from the change in electric resistance, the amounts of corrosion were

successfully obtained in various conditions.

Materials Used

Sulfur compounds used were dibenzyl-disulfide (m.p. 69.0~69.5°C), diphenyldisulfide (m.p. 60.0~60.5°C), didodecyldisulfide (m.p. 32.7~33.5°C), and elementary sulfur. White oils and cetane were used as solvents. The properties of white oil used are shown in Table 1. The thin metal wires used are as follows: Iron wire (piano wire, 0.04 mm in diameter): Stainless steel wire (0.05 mm in diameter).

Table 1 Properties of white oil

Refractive index n_D^{20}	1.4828
Specific gravity 20/4°C	0.8859
Viscosity 100°F cs	80.88
Viscosity 210°F cs	8.43
Viscosity index	77.5
Acid value (mg KOH/g oil)	trace

Prior to the experiment, these wires were vacuum-annealed under conditions of 600°C, 10^{-4} mmHg, and two hours to prevent the variation of electrical resistance by heating and to obtain a good correlation between resistance and temperature. The resistance/temperature characteristics of thin metal wires used are shown in Fig. 2.

Fig. 2 Resistance/Temperature characteristics of used metals

Results

Blank Test

The corrosion process for iron was con-

Fig. 3 Corrosion of iron in white oil containing no sulfur additives (Blank test)

ducted in the white oil without additives at the temperature range from 320°C to 490°C. The experimental results are shown in Fig. 3 and Fig. 4.

There occurred considerable corrosion on the iron wire even in white oil alone. The

Fig. 4 Relation between the square of thickness of iron corroded and the reaction time (Blank test)

amounts of iron corroded were generally increased as the temperature was raised. Fig. 4 shows the relations between the square of thickness of iron corroded and the reaction time. As shown in Fig. 4, it is found that there are the linear relations between them.

Accordingly, the corrosion rates can be expressed by the equation of $(\Delta r)^2 = kt$, where Δr = thickness of iron corroded, t = reaction time and k = rate constant. The data were fitted to the Arrhenius equation, and the calculated value for the apparent activation energy was 21.5 kcal/mole as shown in Fig. 5.

Fig. 5 Dependence of rate constant K on reaction temperature

Elementary Sulfur Solutions

The corrosion procedure for iron was carried out at high temperatures in 0.5 wt% and 0.75 wt% white oil solutions of elementary sulfur, respectively. The experimental results are presented in Fig. 6. The heavier corrosions were observed in elementary sulfur solutions as compared with the blank test, and the corrosion rate apparently depended upon the concentration of elementary sulfur.

There is the same linear relation between thickness of iron corroded and reaction time as in the case of blank test. As shown in Fig. 7, the corrosion rate can be given by the equation of $(\Delta r)^2 = kt + k_0$, where Δr = thickness of iron corroded, t = reaction time, k = rate constant, and k_0 = constant.

The data were fitted to the Arrhenius equation, and the apparent activation energy

Fig. 6 Corrosion of iron in white oil solution of elementary sulfur

Fig. 8 Relation between the square of thickness of iron corroded and reaction time

Fig. 7 Relation between the square of thickness of iron corroded and reaction time (elementary sulfur)

Fig. 9 Relation between the square of thickness of iron corroded and reaction time

Figs. 10 The dependence of rate constant k on reaction temperature

was calculated to be 20.6 kcal/mole regardless of elementary sulfur concentrations (Fig. 5).

Diphenyldisulfide and Didodecyldisulfide

The work of corrosion on the iron was conducted with the white oil solutions which contained diphenyldisulfide or didodecyldisulfide in concentrations of 0.5 wt% and 1.0 wt% as a sulfur respectively. It has been found that there are no remarkable differences between the results of blank test and the corrosion resulted in the solutions of diphenyldisulfide or didodecyldisulfide. And besides, the corrosion rates apparently do not depend on their concentration.

As shown in Fig. 8 and Fig. 9, the corrosion rate can be given by the equation of $(\Delta r)^2 = kt + k_0$, where Δr = thickness of iron corroded, t = reaction time, k = rate constant, and k_0 = constant. Fig. 10 shows the dependence of the rate constant on the reaction temperature for the compounds. The values of apparent activation energy were calculated to be 21.8 kcal/mole for diphenyldisulfide and to be 26.6 kcal/mole for didodecyldisulfide, respectively. These values were given regardless of sulfur concentration.

Dibenzyliddisulfide

The work on the comparative reactivity of dibenzyliddisulfide compared with others was carried out with 0.5 wt%, 0.75 wt% and 1.0 wt% white oil solutions as a sulfur. The experimental results are presented in Fig. 11.

The corrosion rate seemed to follow the

Fig. 11 Corrosion of iron in white oil solution of dibenzyliddisulfide

parabolic law at the initial stage, and after that, there occurred a remarkable increase of corrosion and deviation from the parabolic law. In the region where the corrosion progressed remarkably, it is found that the corrosion rate clearly depends on the concentration of dibenzyliddisulfide. For the initial stage of corrosion, the linear relation seems to exist between the square of thickness of iron corroded and the reaction time, as shown in Fig. 12.

The effect of temperature on the rate

Fig. 12 Relation between the square of thickness of iron corroded and reaction time (Dibenzyl disulfide 0.5%)

Fig. 13 Dependence of rate constant K on the reaction temperature

constant within the region of initial corrosion stage is shown in Fig. 13. The rate constants seem to be fitted to the Arrhenius equation, but the dependence on temperature

does not show good linearity. The apparent activation energy was obtained to be 22.0 kcal/mole regardless of concentrations.

Fig. 14 X-ray analysis of reaction products

Fig. 15 Corrosion of stainless steel in cetane solution of dibenzylidissulfide

X-Ray Analysis of Reaction Products

The results of the x-ray analysis on the reaction products which formed on the thin iron wires are shown in Fig. 14. Fe_3O_4 was identified on the iron wires corroded in white oil. When diphenyldisulfide or didodecyldisulfide was used as an additives, Fe_3O_4 was identified, but FeS could not clearly be detected on the corroded iron wires. FeS was identified on the corroded iron wires in the case of elementary sulfur solutions

Fig. 16 Relation between the cube of thickness of stainless steel corroded and reaction time

or dibenzylidissulfide solutions. Besides, the formation of FeS_2 is observed for the corrosion in dibenzylidissulfide solutions.

Corrosion of Stainless Steel

Fig. 15 presents the experimental results for the corrosion of stainless steel in cetane solutions of dibenzylidissulfide. In the case of stainless steel, it was found that the corrosion rates were very slow compared to that with the iron and there existed no remarkable corrosion which was observed in dibenzylidissulfide solutions after the initial stage.

Apparently, there exists a linear relation between the cube of thickness of stainless steel corroded and reaction time, and the corrosion rate is given by the equation of $(\Delta r)^3 = kt + k_0$, where Δr = thickness of stainless steel corroded, t = reaction time, k = rate constant and k_0 = constant (Fig. 16).

Discussion

Chemical Reactions Involved in Corrosion

Even in white oil alone, considerable corrosion of iron has been found to occur on the wire surface, and Fe_3O_4 was detected there by using the x-ray analysis.

In the corrosion with diphenyldisulfide solutions and with didodecyldisulfide solutions, it has been confirmed that there exist similar amounts of corrosion to that obtained in the white oil without additives and iron oxide, Fe_3O_4 forms as a reaction product. Accordingly, it should be considered that both the oxidation and the sulfurization of iron might take place because of the presence of dissolved oxygen and sulfur compounds in the solution during progressive corrosion. It is difficult to discuss precisely here which reaction is predominant during corrosion. From the data obtained by x-ray analysis, however, the oxidation reaction of iron probably become predominant in this experiment because diphenyldisulfide and didodecyldisulfide might exhibit less reactivity toward iron.

It should be noted from our previous paper that under dynamic conditions, these sulfur compounds behaved to reduce the friction between steel surfaces and the radioactive sulfurized products were identified thereon¹⁾.

On the other hand, the presence of iron sulfide can not be exactly confirmed under static conditions, but these compounds may contribute to the corrosion reaction and may

play a significant role as reactants.

Elementary sulfur and dibenzyl disulfide are much more reactive toward iron, and the sulfurization reaction might come to play an important role.

The chemical reactions involved in the high temperature corrosion with the solutions of sulfur compounds are very complicated and include oxidation reaction, sulfurization reaction and the conversion of oxide to sulfide. Hence, the data obtained here apparently presents the rate of corrosion including oxidation and sulfurization, and it is impossible to distinguish between oxidation and sulfurization, since the reaction products are given as the non-conducting substances.

Reaction Kinetics of Corrosion

The corrosion reaction investigated here is conceivably a kind of tarnishing reaction,

oxidation reaction and/or surface sulfurization reaction would result in the formation of iron-deficient ferrous oxide and/or iron-deficient ferrous sulfide which are produced through the reaction of iron with sulfur compounds or oxygen.

Provided that the generation of iron-ion vacancy would be caused by the formation of iron deficient substances, the surface reaction may be presented as follows:

where, R-S=sulfur compounds, O=dissolved oxygen, $\text{Fe}\square''$ =iron-ion vacancy, $\oplus$ =Positive hole.

- 4) Diffusion of $\text{Fe}\square''$ through formed film.

For instance, the process of surface oxidation of this metal has been studied in great detail⁵⁾, having reached the conclusion that the mig-

Fig. 17 Corrosion mechanism of iron

whose reaction rates are greatly retarded by the formation of barrier products. Consequently, many consecutive reaction steps must be taken into consideration.

As illustrated schematically in Fig. 17, the corrosion process may be visualized as taking place in the following consecutive reaction steps:

- 1) Diffusion of dissolved oxygen or sulfur compounds on the surface of metal wire through the solution.
- 2) Adsorption of dissolved oxygen or sulfur compounds on the surface of metal wire.
- 3) Surface reaction on the metal wire.

Apparently, this surface reaction is very complicated and include oxidation reaction, sulfurization reaction and the conversion of iron oxide to iron sulfide.

It had been assumed that the surface

ration of iron through the iron oxide lattice occurs by diffusion of the Fe^{++} ions through cationic vacancies.

- 5) Surface reaction on the interface between the iron phase and the formed film.

The iron-ion vacancies diffused through the formed film are compensated by iron atoms after reaching the metal phase. The reaction which occurs on the interface, Fe/FeO or Fe/FeS, could be formulated as follows:

In the scope of this investigation, the iron wire alone has been kept at high temperatures in the solution. Therefore it is apparently difficult to assume that steps (1) and (2) are rate-determining steps among the above consecutive reaction steps. It is

impossible to regard step (3) and step (5) as rate-determining steps, because, as the reaction time passes, the amount of corrosion does not increase linearly and the corrosion rate gradually diminishes.

If the diffusion of Fe^{2+} is assumed to be a rate-determining step, the corrosion rate should be inversely proportional to the thickness of formed film and directly proportional to the number of Fe^{2+} on the metal surface.

Assuming that the thickness of corroded iron is directly proportional to thickness of formed film, the corrosion rate is given by the following equation:

$$\frac{d(\Delta r)}{dt} = \frac{k \cdot c}{\Delta r} \quad (2)$$

where, Δr =thickness of iron corroded, t =reaction time, C =concentration of Fe^{2+} on the metal surface, and k =constant.

In the above equation (2), the surface concentration of Fe^{2+} , C , might remain constant under the definite conditions, depending on reaction temperatures, the kinds of sulfur compounds, and their concentrations. The reason is because there might exist the partial equilibrium in the surface reaction as described in the following:

Since the surface concentration of Fe^{2+} is constant, the following equation is obtained by integrating the equation (2):

$$(\Delta r)^2 = kt + k_0 \quad (3)$$

where k , k_0 =constant.

The rate-determining step of corrosion conceivably arises from the diffusion of Fe^{2+} through the formed film, because there are linear relations between $(\Delta r)^2$ and t as obtained in the experimental results (Fig. 4, Fig. 7, Fig. 8, Fig. 9).

In the case of dibenzyl disulfide solutions, the linear relationship is found only in the initial stage, and in the final stage, there occurs remarkable corrosion and crack or cleavage which is optically observed on the wire surface. After the formation of crack or cleavage, it is doubtful whether the amounts of corrosion could be exactly measured, because the values of electric resistance should be varied remarkably. Hence, the remarkable increase of corrosion observed in dibenzyl disulfide might be due to both the unusual increase of electrical resistance and the decrease of reaction barrier caused by the presence of crack or cleavage.

The reason why dibenzyl disulfide exhibits this interesting behavior and forms the crack or cleavage on the surface has not been clarified. However, this behavior not only depends on its chemical reactivity, but also on the peculiar constitution of barrier products, considering that FeS and FeS_2 were identified among the products. Moreover, it has been found that it is more difficult for the crack or cleavage to occur on the film formed at 500°C within some reaction period, as shown in Fig. 11. With stainless steel, there are much smaller amounts of corrosion compared with iron, and the rate of corrosion after the initial stage decreases rapidly with the lapses of reaction time at any temperatures. Furthermore, the parabolic law can not be applied to the relation between amounts of corrosion and reaction time, but there exist clearly the linear relationship between $(\Delta r)^2$ and t . It has been expected that a more complicated reaction occurs through the surface barrier layers. The mechanism of corrosion will not be discussed here.

The Sulfur Compounds as EP Additives

The results obtained at high temperature may be helpful to assume not only the action of sulfur compounds as EP additives, but also the mechanism of general corrosion by sulfur attack.

It should be pointed out that the static condition applied in this investigation is quite different from the dynamic condition where there exists the friction between mating surfaces accompanying with wear. However, the above results make it possible to deduce the action of sulfur compounds under dynamic condition, because high temperatures can be reached locally to contribute to the reaction during friction.

Diphenyldisulfide and didodecyldisulfide may be less effective as EP additives because of their low reactivity even at high temperatures, and elementary sulfur is not so available to use as an additive because of its corrosiveness at ordinary temperature. On the contrary, dibenzyl disulfide becomes remarkably reactive at high temperature region and presents interesting characteristics in which there occurs crack or cleavage.

Under dynamic conditions, dibenzyl disulfide is generally more reactive than diphenyldisulfide, and the former increases remarkably the amount of reaction product as the sliding velocity increases before the

sweeping action of slider which becomes predominant during friction⁶).

Godfrey has recently shown that the sulfurized mineral oil promotes oxidation of steel under EP conditions, and that the coexistence of oxide film and sulfide film may have caused the display of a high load-carrying capacity³. If the above suggestion is correct, following phenomena investigated here would be very interesting in elucidating the mechanism of EP additives: (1) considerable oxidation of metals in white oil alone. (2) the promoting effect of corrosion as a result of formation of crack or cleavage.

Conclusion

The corrosion of metal wires was conducted in hydrocarbon oils containing sulfur compounds to develop the knowledge of EP additives and the general sulfur corrosion at high temperatures.

(1) It has been revealed that corrosion rate of iron follows the parabolic law. Accordingly, the corrosion process is conceivably controlled by diffusion of reactants through barrier products formed on iron surface.

(2) With iron wires, there were con-

siderable corrosion and formation of Fe_3O_4 in the white oil alone. Hence, the chemical reactions involved in corrosion may be very complicated and include oxidation, sulfurization, and the conversion of oxide to sulfide.

(3) Elementary sulfur and dibenzyldisulfide showed the intensive corrosion action on iron. On the contrary, diphenyldisulfide, didodecyldisulfide showed less corrosive action. Besides, dibenzyldisulfide showed particular corrosive action to decrease the reaction resistivity of formed film with cracking.

(4) With stainless steel, corrosion rates were very slow and the corrosion promoting action of dibenzyldisulfide was not observed at any higher temperatures.

References

- 1) Sakurai, T., Ikeda, S., and Okabe, H., *ASLE Trans.*, **5**, 67 (1962).
- 2) Bowden, F.P., and Tabor, D., *The Friction and Lubrication of Solids*, Oxford University Press, London, pp. 33 (1950).
- 3) Barcroft, F.T., *Wear.*, **3**, 440 (1960).
- 4) Godfrey, D., *ASLE Trans.*, **5**, 57 (1962).
- 5) Davies, M.H., and Simnad, M.T., *J. Metals*, **3**, 889 (1951).
- 6) Sakurai, T., Ikeda, S., and Okabe, H., *ASLE Trans.* in press.