

潤滑添加劑로서의 *N*-Iodopyridinium Dichlorodate 의 화학반응성

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Chemical Reactivity of *N*-Iodopyridinium Dichlorodate as a Lubricant Additive

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요 약 소량의 요오드 화합물이 윤활유에 함유될 때 금속표면사이의 마찰을 감소시키고 내마모성을 향상시키는데 이는 금속표면에 박층상구조의 이요오드화물이 형성되기 때문이라고 한다. 그러나 금속표면에서의 화학반응성, 마모와 극압실험 및 hot wire method에 의한 결과에 의하면 윤활기구는 이 요오드화물의 박층상 구조가 아니고 다른 기구에 의한 것임을 알았다. 유기 요오드화합물중에서 특히 *N*-iodopyridinium dichlorodate는 double charge transfer complex로써 다른 methyl iodide계의 화합물 보다 금속표면 사이의 마찰을 더욱 감소시키고 윤활기구는 interhalogen의 화학반응에 의한 것임을 알았다.

Abstract Small amounts of iodine compound in mineral oils are usually effective in reducing friction of metallic surfaces. Such improvement in frictional behaviour of wear characteristics was explained by the formation of a diiodide layer lattice structure at the metallic contact surfaces. The lubrication mechanism, however, by which organoiodine compounds functions is not based on the formation of such lattice structure iodide. It was tested and shown, by a static surface chemical reactivity test, wear and EP tests, and a hot wire method, that compound such as *N*-iodopyridinium dichlorodate, a double charge transfer complex, reacted with metals as an interhalogen compound and that the resultant thin film product reduced appreciable the friction of metallic surfaces, more than compounds such as methyl iodide, diiodomethane, and iodoform.

These results suggest that the action of iodine, included in organoiodine compounds, is not that of a classical layer structure iodide, and an entirely new mechanism may be derived from a further studies on charge transfer complex compounds of organoiodine compounds.

Introduction

It is of interest to note that iodine compound in mineral oils is effective in reducing metallic fric-

tion and improving wear characteristics in the lubrication, even if the compound is restricted to use for its corrosive and toxic properties. Although the mechanism by which iodine function

is not yet known, Owens, Roberts, and Barnes¹ stated the mechanism due to the formation of lamellar structure of diiodide. Further study^{2,3} on the mechanism suggested that surface adsorption and electrical phenomena are involved. Brown and Owens⁴ reacted interhalogen compounds with olefinic materials to develop a non-toxic and non-corrosive iodine additive which is useful at high temperature operation. The work to be described in this paper is a study of chemical reaction between metallic surfaces and few organoiodine compounds. *N*-Iodopyridinium dichlorodate, a double charge transfer complex, was used along other organoiodine compounds to study the frictional behaviour of metallic contact and to understand its mechanism. Few investigations have been made as to the correlation between chemical reactivity and load carrying capacity of oils containing *N*-iodopyridinium dichlorodate.

Experimental

Chemical Reactivity between Metallic Surfaces and Organoiodine Compounds *N*-iodopyridinium dichlorodate, methyl iodide, diiodomethane, and iodoform in mineral oils (equivalent to SAE 30 and 40) were used to react with SUJ 2 steel (C=0.95~1.10 %, Si=0.15~0.35 %, Mn=less than 0.5 %, P=less than 0.025 %, S=less than 0.025 %, and Cr=1.30~1.60 %) and aluminum plates.

N-Iodopyridinium dichlorodate was prepared⁵ by reacting 50 ml of 2 *M* hydrochloric acid with 5 ml of pyridine and 25 ml of 0.05 *M* potassium iodate. Other organoiodine compounds were commercial reagent grade chemicals. Few drops of mineral oil containing a certain amounts of the above additives were heated on a hot pre-polished metallic plate to 200 °C for 2 hours. After the reaction, the metallic surface was flushed with organic solvent and air dried. The surface was

examined with a microscope.

Wear and EP Tests Shell four ball wear tester was used under 40 kg of load and 1200 rpm speed at 75 °C for 10 minutes. Scar diameters on steel balls (AISI-C 52100, AFBMA Grade 25) were examined after each test of oils containing additives. Four ball EP tester (ASTM D 2596) was used to examine the EP characteristics of samples containing additives.

Hot Wire Method^{6,7} Chemical reaction between piano wire surface and additives in mineral oil was examined by Sakurai's hot wire method. A piano wire supported across two terminals was immersed in a sample oil and the electrical resistance of the wire was measured. The wire was pre-heated at 600 °C and 10⁻⁴ mmHg for 2 hours to minimize the change of electrical resistance by heating. The reaction temperature, deduced from the resistance/temperature characteristics of the piano wire, was maintained constant throughout the whole experiment. The amount of corroded material on the wire surface (or the thickness of the wire) was measured from the change in the electrical resistance of the wire by the following equation, assuming the corroded material be non-conducting and the reaction be homogeneous over the entire surface.

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

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

Results and Discussion

A static chemical reactivity between metallic surfaces and the organoiodine compounds in mineral oil was conducted at 200 °C for 2 hours and the results are shown in Fig. 1. It was found that the iodine contents in methyl iodide, diiodomethane, and iodoform did not give great

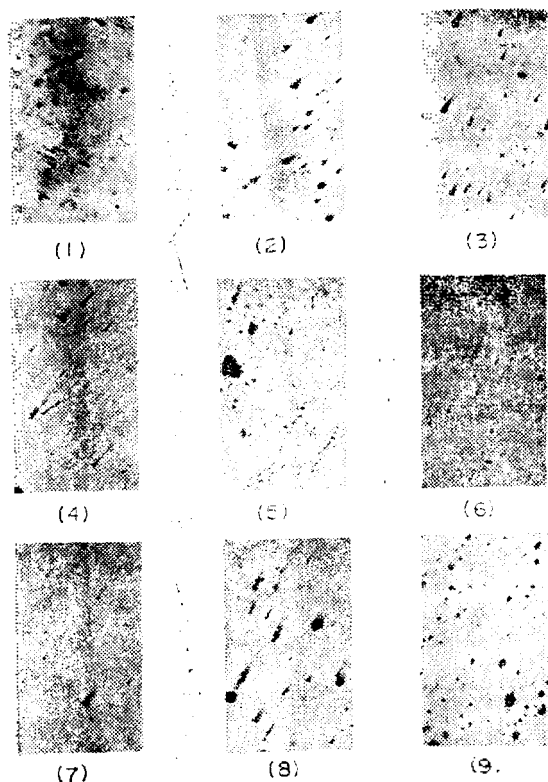


Fig. 1. Bearing metal surface change by organoiodine compounds in oil

- (1) no additive in oil (2) 0.5wt% of CH_2I
 (3) 0.5wt% of CH_2I_2 (4) 0.5wt% of CHI_3
 (5) 0.5wt% of $\text{C}_5\text{H}_5\text{NI}_2\text{Cl}_2$
 (6) 0.75wt% of CH_2I (7) 0.75wt% of CH_2I_2
 (8) 0.75wt% of CHI_3 (9) 0.75wt% of $\text{C}_5\text{H}_5\text{NI}_2\text{Cl}_2$

effect on the chemical reactivity of metallic surfaces as shown in Fig. 1-(2), (3), and (4). The increase of the amounts of these compounds also did not affect the chemical reactivity as shown in Fig. 1-(6), (7), and (8). The metallic surfaces are almost the same as those of Fig. 1-(2), (3), and (4). In other words, the degree of chemical reaction of those compounds is almost the same. However, *N*-iodopyridinium dichlorodate in mineral oil reacted deeply with metallic surfaces and the degree of chemical reaction increased as shown in Fig. 1-(5) and (9). It was assumed that the

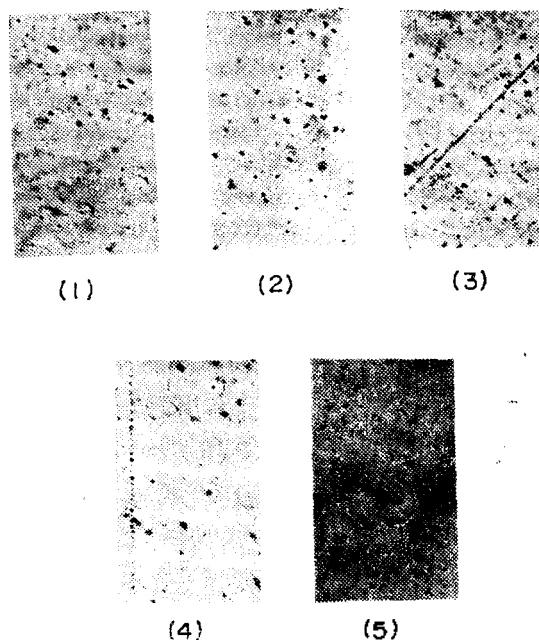


Fig. 2. Aluminum metal surface change by organoiodine compounds in oil

- (1) no additive in oil (2) 0.75wt% of CH_2I
 (3) 0.75wt% of CH_2I_2 (4) 0.75wt% of CHI_3
 (5) 0.75wt% of $\text{C}_5\text{H}_5\text{NI}_2\text{Cl}_2$

metallic surfaces reacted with *N*-iodopyridinium dichlorodate and produced an interhalogen compound.

The reaction of organoiodine compounds with an aluminum surface was next observed. The chemical reaction was more active and gave more corroded surfaces than using steel surfaces as shown in Fig. 2. It is assumed that the product is AlI_3 which is a three dimensional complex and does not have a layer structure. *N*-iodopyridinium dichlorodate, which is considered to be a kind of interhalogen compounds and very similar to the free halogens, oxidized aluminum surfaces more than other organoiodine compounds, probably giving a product of polyhalide mixture $-\text{AlI}_3$ and AlCl_3 .

The wear and EP characteristics of organoiodine compounds in mineral oils were demonstrated as described before and the results are shown in

Table 1. Wear test of organoiodine compounds.

Compound	Contents in SAE 30 (wt %)	Scar diameter (mm)	Contents in SAE 40 (wt %)	Scar diameter (mm)
Blank		0.978		1.890
CH ₃ I	0.05	0.808	0.25	0.916
	0.25	0.976	0.75	0.824
	0.50	0.784		
CH ₂ I ₂	0.05	1.004	0.25	0.824
	0.25	0.992	0.75	0.816
	0.50	0.792		
CHI ₃	0.005	0.988	0.038	0.912
	0.05	0.892	0.075	0.848
	0.10	0.668		
C ₅ H ₅ NI ₂ Cl ₂	0.0025	0.948	0.075	0.888
	0.005	0.960	0.110	0.736
	0.025	0.716		
	0.05	0.864		
	0.10	0.896		

Tables 1 and 2. In general, the scar diameter became smaller as the amounts of additives increased and the load at welding increased. However, much larger amounts of additives were necessary to get the same order of scar diameter as *N*-iodopyridinium dichloroate, and the same effect could be seen in the load carrying capacity tests.

Freeman⁸, using phosphorus and sulfur, and Klaus⁹, using tricresyl phosphate, explained the mechanism of frictional behaviour as the formation of thin film which resembles to the structure of MoS₂, BN₃, WS₂, TiI₂, and graphite, besides the nature of the surface modification and the influence of the underlying metal structure. However, from our results and by Furey² who tested glass ball on glass with iodine as an additive, the explanation can not be true, and there must be another explanation on the mechanism.

The influence of the viscosity of mineral oils (e.g., the viscosity of SAE 40 at 210 °F is 70

Table 2. EP test of organoiodine compounds

Compound	Contents in SAE 30 (wt %)	Welding load (kg)
Blank		100
CH ₃ I	0.005	100
	0.25	100
	0.50	110
CH ₂ I ₂	0.005	115
	0.25	140
	0.50	160
CHI ₃	0.005	100
	0.05	100
	0.10	120
C ₅ H ₅ NI ₂ Cl ₂	0.0025	100
	0.005	110
	0.025	120
	0.05	160
	0.10	190

~85 sus and the viscosity of SAE 30 at 210 °F is 58~70 sus) to the wear scar diameter is also shown in the Table 1, and it was found that

Table 3. Degree of corrosion of organoiodine compounds by hot wire method.

Reacting time, min	Change in thickness $\Delta r \times 10^3$ cm			
	CH ₃ I	CH ₂ I ₂	CHI ₃	C ₅ H ₅ NI ₂ Cl ₂
10	1.03	2.90	N. C.	1.30
20	1.10	2.92	N. C.	2.10
40	1.10	2.02	N. C.	2.67
60	1.33	3.66	N. C.	4.95

N. C. = no change

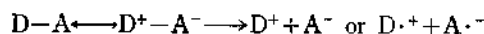
the larger the viscosity the smaller the scar diameter.

The corrosion process of piano wire was conducted in the base oil alone and in the oils containing various organoiodine compounds at high temperature. Table 3 shows the experimental results obtained for the various samples. Since the resistance for blank sample was smaller than the initial resistance, giving a negative value of Δr , the fact that a small change in wire thickness ($\Delta r = -6 \times 10^{-4}$ cm) suggested no reaction occurred for the blank sample. The degree of corrosion, in general, increased as the reacting time increased, giving increased values of Δr . We expected that the chemical reactivity of *N*-iodopyridinium dichlorodate and methyl iodide would be greater than that of diiodomethane and chloroform. The results showed that the order of chemical reactivity is C₅H₅NI₂Cl₂ > CH₂I₂ > CH₃I > CHI₃, and it was concluded that the most active additive is *N*-iodopyridinium dichlorodate. Besides, *N*-iodopyridinium dichlorodate is an interhalogen compound and will react with olefinic materials, hydrolyzing the reaction products to an equilibrium mixture, forming a non-toxic and non-corrosive additive.

The chemical reactivity of *N*-iodopyridinium dichlorodate, a charge transfer complex and a polyhalide compound, is similar to that of X-X' type interhalogen compound. The X-X' type of compound has larger polarity than free halogen elements due to the large difference in electrone-

gativity, and its oxidation characteristics (toward metal or nonmetal compounds) and hydrolyzing property are similar to those of free halogen elements.

Let (C₅H₅NI)⁺(ICl₂)⁻ be D⁺-A⁻ then



and



When we let the wave function of D-A and D⁺+A⁻ be Ψ_0 and Ψ_1 , respectively, the wave function of the compound at the ground state becomes its linear combination.

$$\Psi_N = a\Psi_0 + b\Psi_1$$

where $a^2 + b^2 = 1$ and $a \gg b$.

For the ground state, $H\Psi_N = E_N\Psi_N$

where the Hamiltonian becomes as follows,

$$H = \sum_i H_i^{\text{core}} + \sum_{i>j} \frac{e^2}{r_{ij}}$$

$$H_i^{\text{core}} = - \left(\frac{\hbar^2}{8m\pi^2} \nabla_i^2 + \sum_r \frac{e^2 z_r}{r_{ir}} \right)$$

Integrating the above equation

$$\int_{-\infty}^{\infty} \Psi_N H_N dv = E_N \int_{-\infty}^{\infty} \Psi_N^2 dv$$

or

$$\int (a\Psi_0 + b\Psi_1) H (a\Psi_0 + b\Psi_1) dv$$

$$= E_N \int (a\Psi_0 + b\Psi_1)^2 dv$$

If

$$\int \Psi_0 H \Psi_0 dv \equiv H_{00} \equiv H_{10}$$

$$\int \Psi_0 H \Psi_0 d\tau \equiv H_{00} = E_0 \int \Psi_0^2 d\tau \equiv E_0$$

then

$$a^2 E_0 + b^2 E_1 + 2ab H_{10} = (a^2 + b^2 + 2abs) E_N$$

$$2a E_0 + 2b H_{10} = 2a E_N + 2bs E_N$$

Differentiating with respect to a and b and let the resultant be zero, the determinant becomes as follows,

$$(E_0 - E_N)a + (H_{10} - sE_N)b = 0$$

$$(H_{10} - sE_N)a + (E_1 - E_N)b = 0$$

$$\therefore E_N = E_0 - \frac{(H_{10} - sE_N)^2}{E_1 - E_0}$$

$$\cong E_0 - \frac{(H_{10} - sE_N)^2}{E_1 - E_0} = E_0 - R_N$$

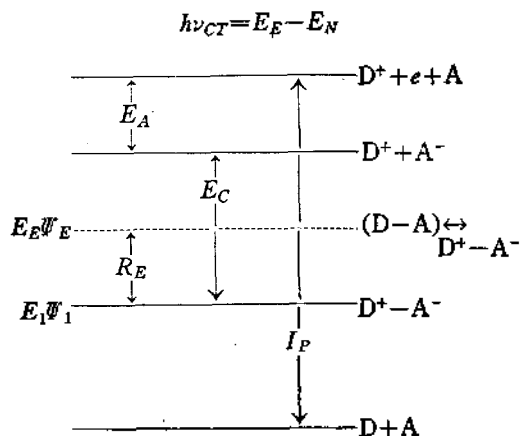
For the excited state,

$$\Psi_E = -b\Psi_0 + a\Psi_1$$

and similarly to previous treatment

$$E_N \cong E_1 + \frac{(H_{10} - sE_1)^2}{E_1 - E_0} = E_1 + R_E$$

The graphical explanation of energy [is] shown in the diagram, and the transition from the ground state to the excited state, $h\nu_{CT}$, becomes as follows



From the graph, the energy level of HOMO, I_p , can be calculated by Hückel's MO theory.

A linear relationship between $h\nu_{CT}$ and I_p is obtained,

$$h\nu_{CT} = E_E - E_N$$

$$= I_p - E_A + E_C - E_C + R_N$$

$$= I_p - E_A - C$$

where E_A is an electron affinity and E_C is a Coulombic energy. E_A is an energy level of LOMO and can be calculated or expressed as follows,

$$E_A = -(\alpha + m_{m+1})\beta$$

The future study on the chemical reactivity of the compound will include work on bond order, free valence, and electric charge, those are deduced from the calculation of coefficients of AO in MO.

Conclusion

The chemical reactivity of *N*-iodopyridinium dichloroate, observed from the reaction between some organoiodine compounds and bearing metal and aluminum surfaces, wear and EP tests, and corrosion test of hot wire method, was found to be greater than that of other organoiodine compounds.

The reaction product of *N*-iodopyridinium dichloroate, considered as an interhalogen compound, is assumed to be a mixture of polyhalide and the thin film of this mixture reduced the frictions of metallic surfaces.

Since the conventional theory of thin layer structure of diiodide does not hold true in our work, a new mechanism must be explained.

Molecular orbital study of *N*-iodopyridinium dichloroate, a double charge transfer complex, will predict its chemical reactivity in terms of bond order, free valence, and electrical charge.

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