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The effect of surface oxide layers on the oxidative behaviour of imidazole-treated copper

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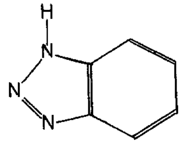
Molecular structure and degradation mechanisms of undecylimidazole on copper oxide was studied using Fourier transform reflection-absorption spectroscopy. Undecylimidazole suggests the random amorphous orientation on a non-preoxidized surface, semicrystalline random orientation on copper preoxidized at 150° C for 30 min, and parallel orientation of the imidazole ring to the surface on copper preoxidized at 230° C for 30 min. The difference in morphology and orientation of undecylimidazole on oxide is due to the reactivity of the imidazole and the substrate surface, the rate of deposition of the imidazole, and the evaporation rate of solvent from the solution placed on the surface. The degradation is catalysed by two types of copper; in the film and substrate. The rate-determining step of the degradation is the reactivity of the carboxylic acid produced in the intermediate step of the degradation and the surface oxides. Molecular oxygen is necessary for the degradation which takes place initially from the outer layer of the film by the catalytic effect of the copper in the film.

1. Introduction

Benzotriazole (BTA) (I) is widely used as an inhibitor for copper and copper alloys [1–7]. Some imidazoles have also recently been used as useful inhibitors [8–12]. The molecular structure and anti-corrosion mechanism of benzotriazole have been studied by many authors but are still not well understood [13–18]. On the other hand, it is only very recently that the molecular structure of benzimidazoles (II) on copper surfaces has been investigated [19–21].

Imadazole compounds are becoming very important as corrosion inhibitors of metals. They appear to be somewhat similar to benzotriazoles in forming barrier compouds by reaction with surface oxides. Their protective nature depends on whether they are amorphous or crystalline compounds. We have studied imidazoles having long alkyl groups, because they can be accumulated quickly on the copper surface from acidic aqueous solution due to the fast chemical reaction of the imidazole ring and van der Waal's force of the alkyl group [25]. The fast film formation is an important factor for corrosion protection because a thick and dense complex film is believed to act as a protective barrier for the underlying copper. We have studied the molecular structure and thermal stability of undecylimidazole (III) on freshly polished copper [22, 24].



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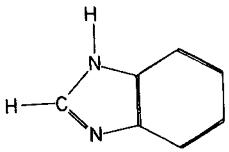

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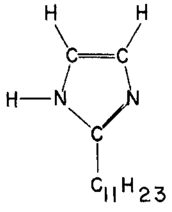

(III)

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It is now widely accepted that the presence of metal oxide is a key factor in the mechanism of corrosion protection [18]. In this paper we shall describe the molecular structure and thermal stability of undecylimidazole with respect to the effect of the surface oxide layers. No paper has been published on this subject except for the thermal stability of BTA. Studies on benzotriazole provide valuable reference information because of the structural similarity with imidazole. Roberts [16] found that the surface film formed on Cu_2O was a mixture of Cu(I)BTA and Cu(II)BTA. The relative amount of Cu(II)BTA increased with longer exposure time to acqueous BTA solution at 60° C. Chadwick and Hashemi [17] have shown X-ray photoelectron spectroscopy (XPS), that the surface film formed on copper and Cu_2O *in situ* is a Cu(I)BTA species under a wide variety of conditions and that any Cu(II) is produced by surface oxidation removal from the liquid phase. Ogle and Poling [26] have mentioned that Cu(II)BTA species resulted from partial oxidation of the initially formed Cu(I)BTA and that surface films formed in NaCl containing BTA solution are predominantly Cu(I) with approximately 10% Cu(II). Fox *et al.* [18], using XPS, have also found that the complex formed on the surface of Cu_2O is Cu(II)BTA, but the molecular structure of the complex on CuO is more complicated. The change of Cu(I)BTA to Cu(II)BTA was attributed to the instability of the Cu(I)BTA in air [17]. Many simple Cu(I) compounds are easily oxidized to Cu(II) by exposure to air [27–29].

It has been postulated that Cu(I)BTA takes a polymeric form [1, 16]. Notoyama and Poling [30], using electron microscopy, have found that CuBTA formed on relatively thin Cu_2O films has a star-like structure of acicular crystallites. On the other hand, the CuBTA crystallites formed on Cu_2O films more than 20 nm thick and a more matt structure. The molecular structure of Cu(II)-BTA is not well understood, but the molecular organization has been assumed to be dictated by the geometric requirement of tetrahedral coordination in the Cu(I) complex and square planer on octahedral coordination of CuO-covered surfaces [18, 31]. BTA has different chemical reactivities towards copper, Cu_2O and CuO. The adsorption of BTA on Cu_2O is rapid, whereas adsorption on CuO is very slow [3, 17]. Using ellipsometry, Mansfeld and Smith [32] have found that BTA interacts with copper only when it is covered with oxide.

Degradation of undecylimidazole on copper was reported in our previous paper [24]. Most imidazoles alone are thermally stable [33], hence it is reasonable to assume that the imidazole is catalytically degraded on the copper surface. Catalytic oxidation of organic compounds by copper or copper oxide have been reported [34–39]. Anshits *et al.* [40] have studied the oxidation of alkenes and alkynes on Cu_2O at 200° C and postulated the degradation mechanism. The rate-determining step is the decomposition of surface carboxylate species by O_2. As the temperature increases, the mechanism changes to another in which the rate-determining step is the first interaction between hydrocarbon and catalyst with cleavage of a C–H bond. They also compared the reactivity of 1-alkenes, 1-alkynes and C_6 hydrocarbons over CuO at 300° C [41].

The selective oxidation of propylene to acrolein over transition metal oxide catalysts including copper oxide has been studied extensively [42–44]. It is now widely accepted that the oxidation of propylene proceeds via the formation of a symmetric allylic intermediate [45]. This allylic species reacts with oxygen from the oxide lattice after a second hydrogen abstraction to form acrolein or with a gas-phase or adsorbed oxygen to form acrolein via the decomposition of an alkylperoxide or hydroperoxide [46]. Using the mixed oxide catalyst, it is indicated that propylene is adsorbed on only one type of active site which is energetically similar for all the selective oxidation catalysts tested [43]. Akimoto *et al.* [42] have found that the reaction of isobutylene with Cu_2O at 340° C in the absence of gaseous oxygen does not give methacrylaldehyde. A rapid decrease in selectivity for methacrylaldehyde formation was observed when the adsorbed oxygen was eliminated from the copper catalyst. They concluded that the incorporation of oxygen species into methacrylaldehyde proceeded through a nucleophilic addition of adsorbed electronegative oxygen species via π-allyl formation on Cu^+ in the case of the copper catalyst.

On the other hand, it is known that polyolefins in contact with the copper surface often undergo accelerated thermal oxidation [47–49] where the catalytic oxidation mechanism is different from that of alkene. This mechanism is considered to be free-radical-initiated autoxidation comprising initiation, propagation and termination steps. In general, the metal catalyst for the oxidation accelerates the rate of initiation [50]. Allara and Chan [51] have studied heterogeneous copper-catalysed oxidation of polyethylene and have concluded that the most possible initiation mechanism involves the decomposition of hydroperoxides to free radicals. For these reactions, the metal can be considered as a redox centre, either accepting or donating an electron.

2. Experimental details

The 2-undecylimidazole ($C_{11}Z$), which was supplied by Shikoku Chemicals Company, Japan, was recrystallized in ethanol twice and used for the experiment. A certain thickness of the imidazole film was formed on the copper surface by adding 0.00169 $\mathrm{mol\,l^{-1}}$ undecylimidazole ethanol solution. The di-undecylimidazolat copper II was synthesized in acidic aqueous solution. The compounds were precipitated in the solution by raising the pH using aqueous NaOH solution. The precipitate was washed with ethanol and distilled water repeatedly and then dried in a vacuum oven at 80° C for 3 h. Elemental analysis is shown below. The slight difference between the calculated and found values is possibly due to the residual NaOH.

Calculated		Found	
C	66.4%	C	64.98%
H	9.9%	H	9.18%
N	11.1%	N	10.74%
Cu	12.5%	Cu	12.32%

The heat-treatment of samples was carried out in a mechanical convection oven. The preparation of copper substrates and the optical arrangement of the Fourier transform reflection-absorption attachment were mentioned in our previous papers [23, 24]. All surface reflection spectra were obtained by digitally subtracting the spectrum of clean metal from the metal with adsorbents. The ΔA shown beside the spectrum indicates the difference between the maximum and minimum adsorbance of the spectrum, which is approximately equal to R/R_0, where R represents the reflectivity when ΔA is small.

3. Results and discussion

3.1. Molecular structure of undecylimidazole on copper oxide

The reflection-absorption spectra of preoxidized copper substrates after heating at 150° C for 30 min and 230° C for 30 min are shown in Fig. 1 as spectra A and B, respecitvely. The bands around 645 and 550 $\mathrm{cm^{-1}}$ are assigned to Cu_2O and CuO, respectively [52, 53]. Ishida *et al.* [54] analysed the surface species of oxidized copper surface using FT-IR and ESCA. They found that the surface species of copper substrate oxidized at 150° C for 30 min are Cu_2O approximately 5.0 to 10.0 nm thick. On the other hand, a thin CuO film (less than 5.0 nm) was formed on the surface by heating at 200° C for 30 min and below the CuO film a thicker Cu_2O (20.0 to 25.0 nm) film was observed. They mentioned that the thickness of both CuO and Cu_2O films was increased by heat-

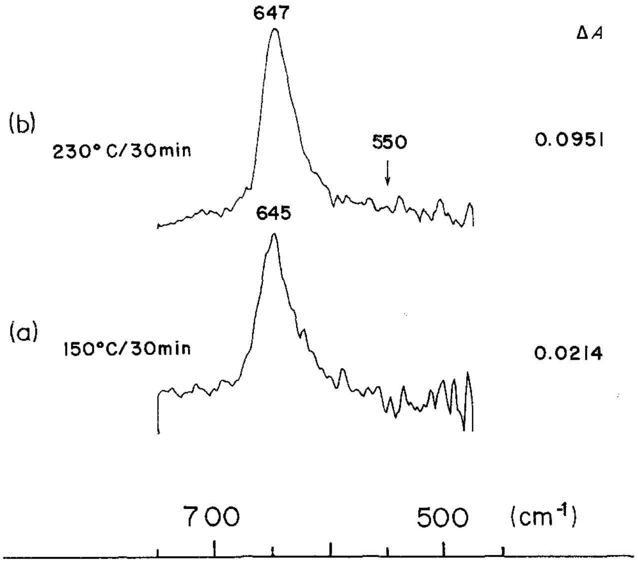


Figure 1 Reflection-absorption infrared spectra of copper heated at: (a) 150° C for 30 min; and (b) 230° C for 30 min.

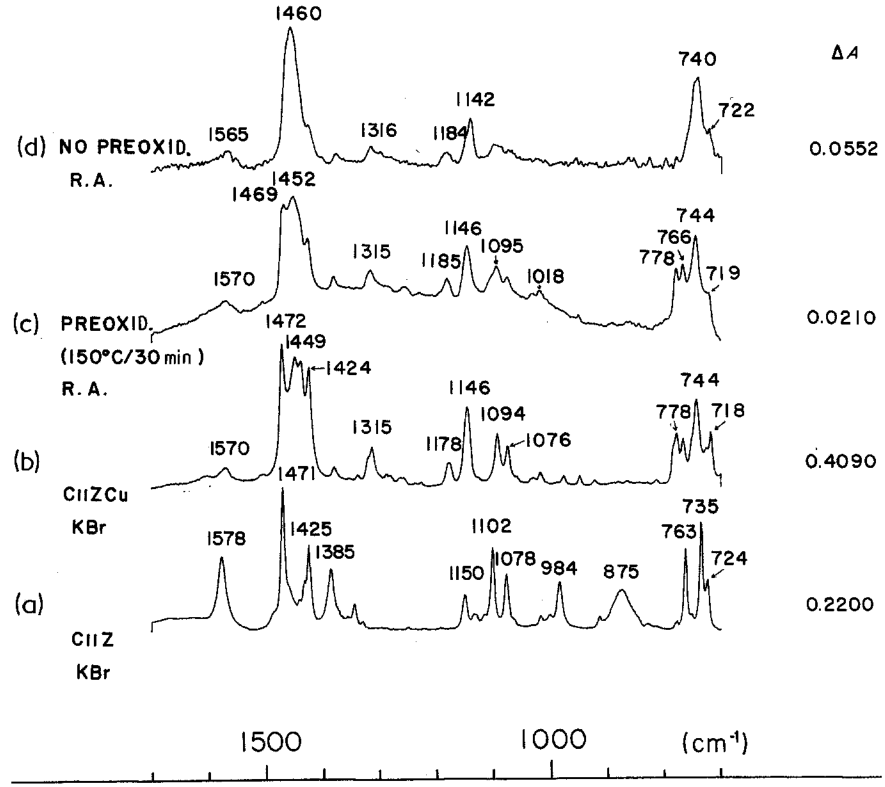


Figure 2 Transmission infrared spectra of: (a) undecylimidazole; and (b) di-undecylimidazolat copper II in KBr pellets. Reflection-absorption infrared spectra of 150 nm thick: (c) undecylimidazole on the preoxidized substrate at 150° C for 30 min; and (d) undecylimidazole on non-preoxidized substrate.

ing at 250° C compared to the 200° C treatment. Therefore, it is reasonable to assume that spectrum A represents mainly Cu_2O and spectrum B is of a thin CuO film with a thicker Cu_2O film below.

The transmission spectra of undecylimidazole and di-undecylimidazolat copper II are shown as spectra A and B in Fig. 2, respectively. The reflection-absorption spectra of 150 nm thick undecylimidazole film on the preoxidized copper at 150° C for 30 min and the freshly polished copper are shown as spectra C and D, respectively. Detailed band assignments will be carried out elsewhere [55]. The molecular structures of imidazole and methylimidazole metal complex have been reported to be crystalline [31, 56]. The hydrocarbon chain is also known to possess a crystalline structure [57]. Therefore, di-undecylimidazolat copper II is expected to have a relatively high crystallinity. Bands around 778 cm^{-1} which disappear in the melt can be regarded as the crystalline bands [55]. The band shapes in the region 1472 to 1421 cm^{-1} also change by melting: several overlapped bands become one relatively broad band with a shoulder [55]. These two regions are useful indicators for the change in morphology.

Fine structures observed around 1452 and 778 cm^{-1} in spectrum C, Fig. 2, indicate that the imidazole complex is slightly crystalline. On the other hand, spectrum D in Fig. 2 shows a rather amorphous structure. The observed difference in crystallinity is likely due to the variation in chemical reactivity between undecylimidazole and the surface oxide layers. Undecylimidazole accumulates more quickly on a slightly preoxidized copper than freshly polished copper [58], indicating a higher reactivity of Cu_2O rather than copper toward the imidazole. A similar trend was observed in the chemical reactivity of BTA and copper or copper oxides [3, 17]. The semicrystalline structure may be obtained only when the reaction speed of the imidazole and copper ions is faster than the deposition speed. This reaction may be much faster than the evaporation rate of the solvent and the imidazole molecules may still possess mobility to form the crystalline structure.

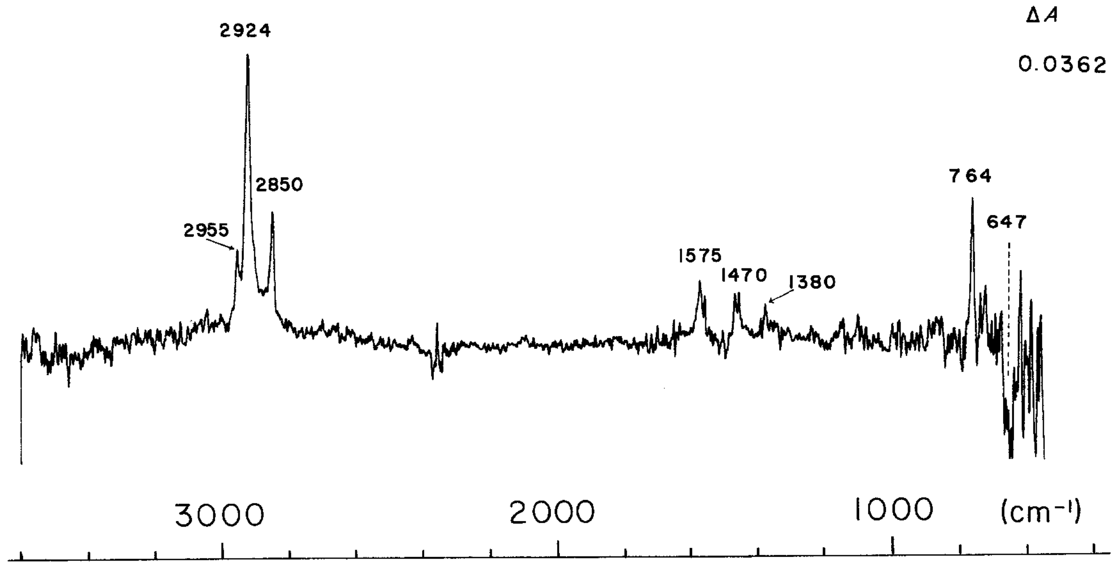


Figure 3 Reflection-absorption infrared spectrum of 50 nm thick undecylimidazole on the preoxidized copper at 230° C for 30 min.

A relatively uniform depth profile of the molecular arrangement supports this statement [55].

If the rate of reaction is slower than the rate of deposition, the migrating copper ion disturbs the crystalline structure initially formed, resulting in the amorphous structure.

The reflection-absorption spectrum of the 75 nm thick films on the preoxidized copper (230° C for 30 min) are shown in Fig. 3. Fig. 3 was obtained using a TGS detector in order to observe copper oxides bands below 650 cm^{-1}, which resulted in a lower signal-to-noise ratio compared to the spectra in Fig. 2, where a sensitive, narrow band-pass MCT detector was used.

Quite different from spectra C and D in Fig. 2 is the spectrum in Fig. 3 which resembles that observed on a gold surface in terms of the imidazole ring [22]. While the alkyl group showed a nearly perfect parallel orientation of the molecular axis to the gold surface, Fig. 3 shows a poor orientation. The orientation in spectra C and D in Fig. 3 are random, because the relative intensity of two bands having perpendicular directions of dipole moment to each other is almost the same as the KBr transmission spectrum of the complex collected from the copper surface [22]. The characteristic feature of the reflection-absorption spectroscopy is that only the dipole moment change perpendicular to the metal surface can be observed in the spectrum [59, 60]. Therefore, this technique provides information on orientation.

The reduction of the Cu_2O band at 647 cm^{-1} in Fig. 3 indicates the reaction of the Cu_2O film with the imidazole ring even though the ring shows flat orientation. This is probably due to the very low reactivity of the imidazole and CuO which is formed on the surface of Cu_2O. The deposition speed is much faster than the reaction speed and, therefore, the reaction takes place slowly after the formation of relatively hard films. The essential difference between spectrum D in Figs. 2 and 3 is the first layer on the substrate. The chemical composition of the first layer on freshly polished copper is possibly $Cu(I)C_{11}Z$ complex at the initial stage of oxidation, because thin Cu_2O is formed very quickly by exposure of copper in air [54, 61].

The crystalline requirement of the Cu(I) complex is tetrahedral coordination whereas square planer or octahedral coordination is required for the Cu(II) complex [18]. Therefore, the random orientation of the molecule on freshly polished copper is likely due to the tetrahedral coordination of Cu(I) complex, and the flat orientation of the molecule on the preoxidized copper (at 230° C for 30 min) is due to either square planer coordination of the Cu(II) complex or inert reactivity of the imidazole on the CuO surface. The orientation of the accumulating molecule without reaction is possibly influenced by one of the first layers. Therefore, the orientation of the imidazole molecules on the freshly polished copper and the preoxidized copper (at 230° C for 30 min) tend to be random and flat, respecitvely, in the early stages of film formation, where the reaction has not progressed extensively.

3.2. Degradation of undecylimidazole film on copper oxide

Approximately 50 nm thick films were placed on differently preoxidized copper substrates and additionally heated at certain temperatures for 15 min. The spectra observed on freshly polished copper, on copper preoxidized at 150° C for 30 min, and at 230° C for 30 min are shown in Figs. 4 to 6, respectively. The thermal degradation process of undecylimidazole on freshly polished copper was studied in detail at 80 to 150° C [24]. The reduction of the CH_2 stretching modes around the 3000 to 2800 cm^{-1} region indicates the elimination of the alkyl group from the molecule, which was observed in relation to the reduction of the imidazole ring vibration mode at 1145 cm^{-1}. The change in bands in the region of 1750 to 1300 cm^{-1} is mainly due to the carbonyl and imide vibration modes of the degradation compound and the band at 2182 cm^{-1} was assigned to the nitrile band of the final degradation compound. The Cu_2O band appeared by additional heating above 180° C in Figs. 4 and 5, and no significant production was observed on the copper preoxidized at 230° C for 30 min up to 210° C. This is due to the preoxidation condition of substrates. The intensity of each band on the copper preoxidized at 230° C for 30 min is much lower than that on non-preoxidized copper, indicating the influence of the optical constants of Cu_2O and CuO films on reflectivity.

The relative intensity of the carbonyl band at 1580 cm^{-1} and the CH_2 band at 2925 cm^{-1} is a good indicator for the comparison of the degradation process. In Fig. 7, a faster increase in the carbonyl band and/or faster decrease in the CH_2 band were observed on non-preoxidized copper. As the oxide film becomes thicker, the relative intensity decreases, indicating a reduced rate of degradation on copper oxide. The limited regions of the spectra obtained by the additional heat-treatment at 150° C for 15 min on differently preoxidized copper substrates are compared in Fig. 8. The imidazole ring vibration mode at 1140 cm^{-1} almost disappeared on freshly polished copper substrate, while it remains on the preoxidized substrates. It is obvious that the degradation proceeds faster on the less oxidized copper surface. Reduction of the CH_2 stretching band by the additional heat-treatment is plotted in

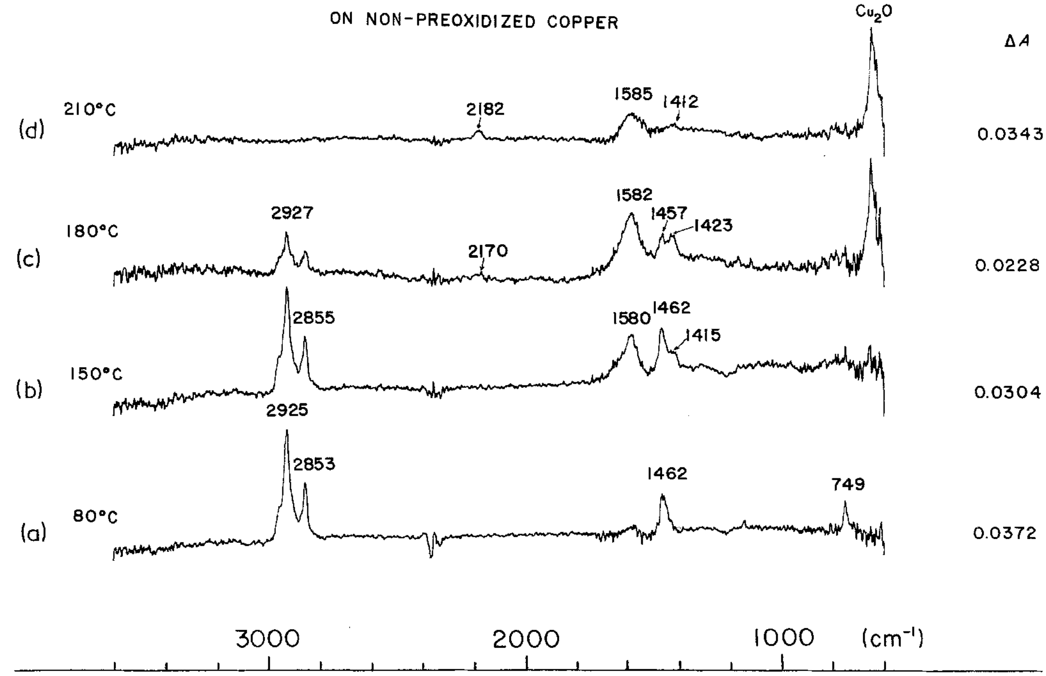


Figure 4 Reflection-absorption infrared spectra of 50 nm thick undecylimidazole on non-preoxidized copper after additional heating for 15 min at: (a) 80° C; (b) 150° C; (c) 180° C; and (d) 210° C.

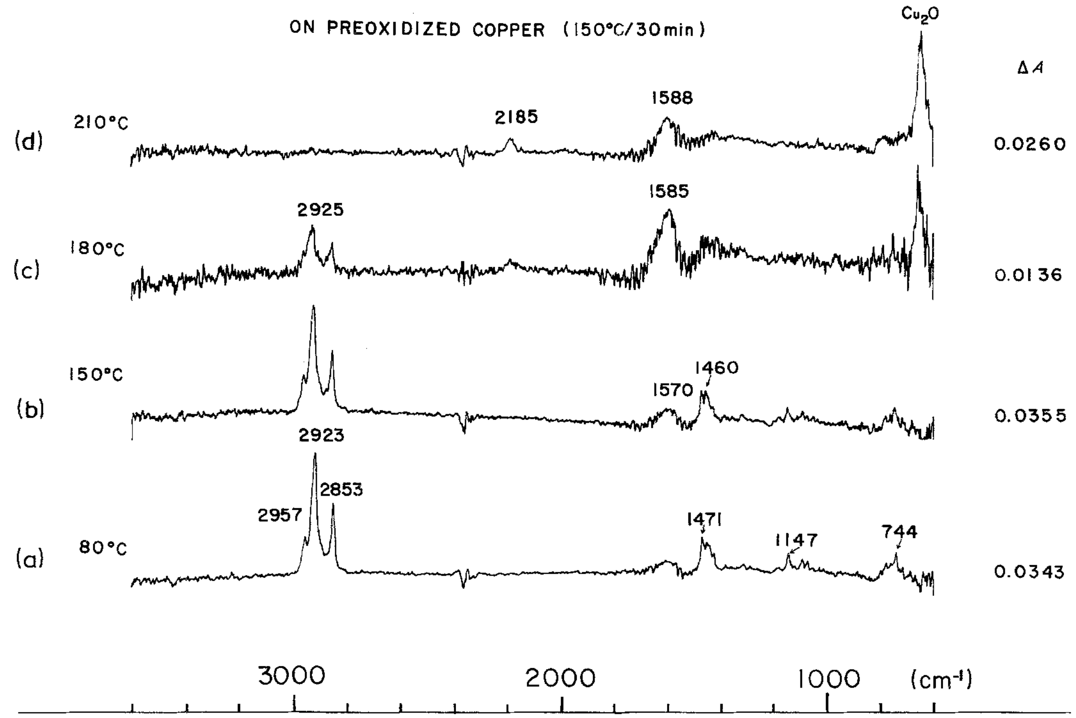


Figure 5 Reflection-absorption infrared spectra of 50 nm thick undecylimidazole on preoxidized copper at 150° C for 30 min after additional heating for 15 min at: (a) 80° C; (b) 150° C; (c) 180° C; and (d) 210° C.

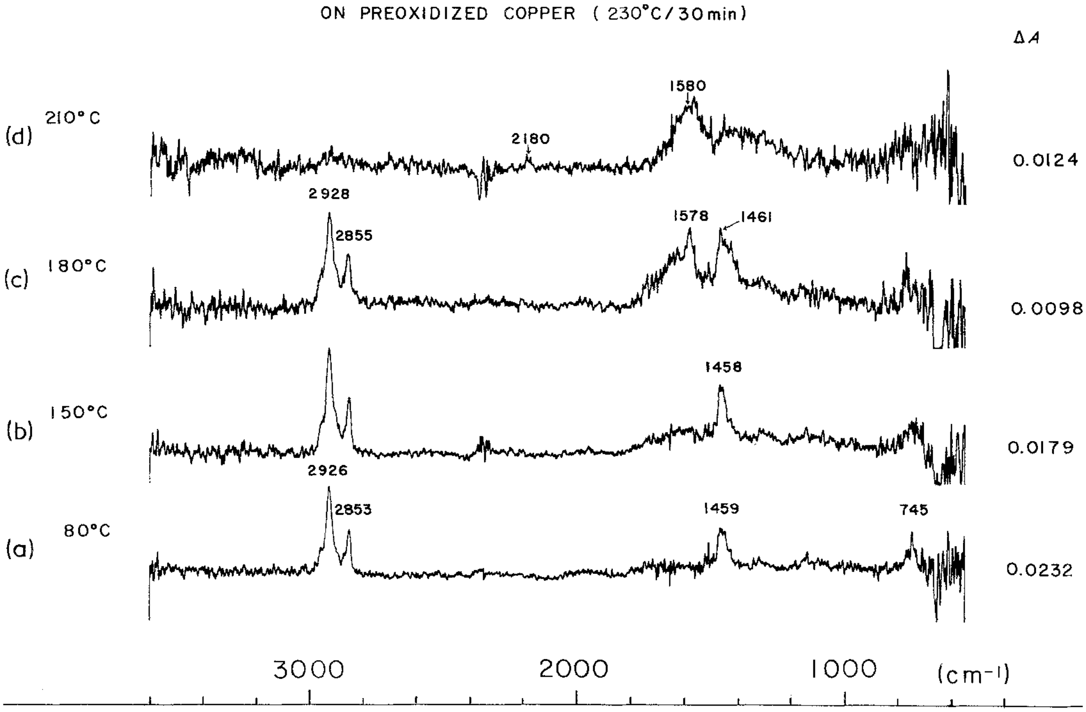


Figure 6 Reflection-absorption infrared spectra of 50 nm thick undecylimidazole on preoxidized copper at 230° C for 30 min after additional heating for 15 min at: (a) 80° C; (b) 150° C; (c) 180° C; and (d) 210° C.

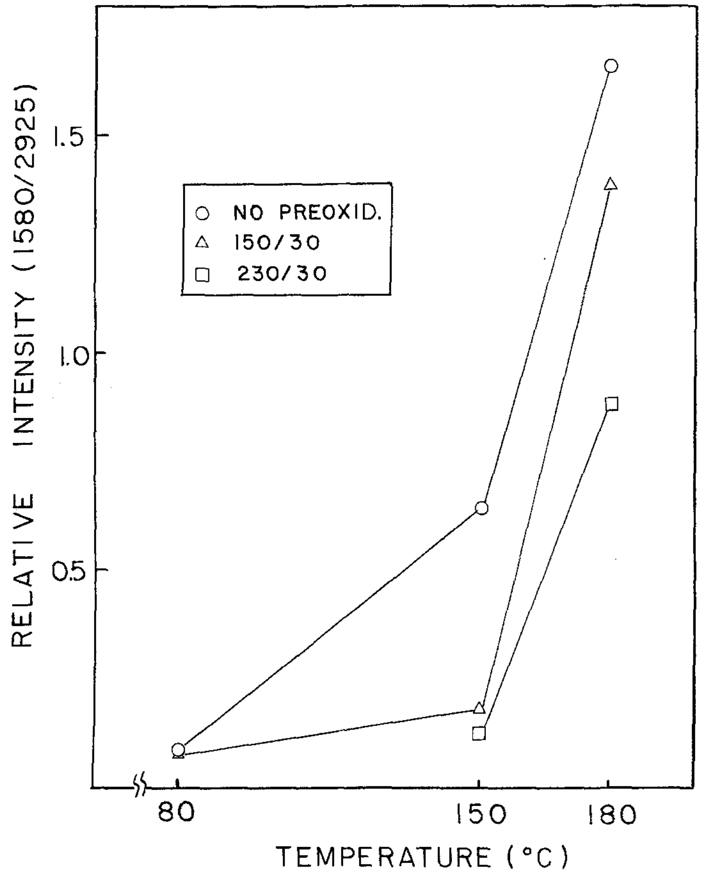


Figure 7 The relative intensity of bands at 1580 and 2925 cm^{-1} plotted against additional heating temperature.

Fig. 9. The freshly polished copper has the strongest catalytic effect while the copper preoxidized at 230° C for 30 min, in which CuO exists in the outermost layers showed the least effect. These results probably reflect different degradation rates of undecylimidazole on CuO_2 and CuO.

The production of the initial carbonyl groups was postulated based on the photo-oxygenation process in our previous paper [24]. However, photo-oxygenation of imidazoles is carried out at low temperatures (10 to 100° C) with the presence of a sensitizer such as tetraphenylporphyrin or

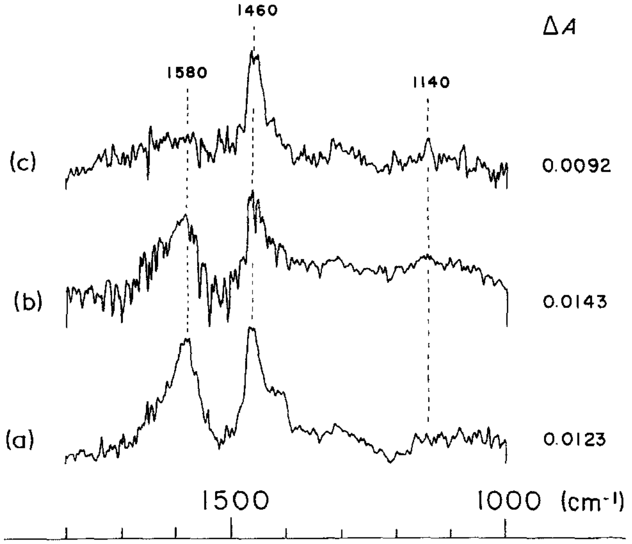


Figure 8 Reflection-absorption infrared spectra of 50 nm thick undecylimidazole after additional heating at 150° C for 15 min on: (a) non-preoxidized copper; (b) preoxidized copper at 150° C for 30 min, and (c) preoxidized copper at 230° C for 30 min.

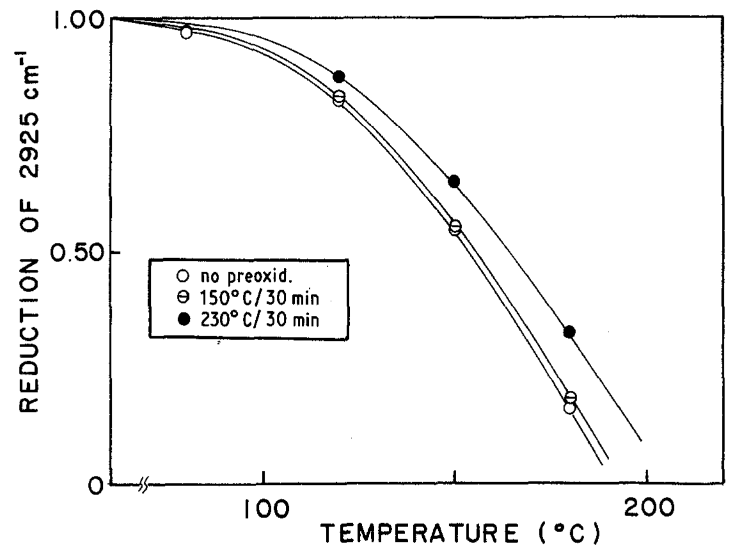
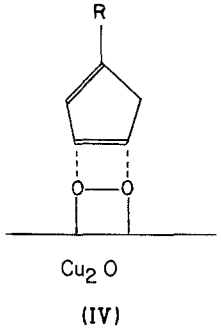


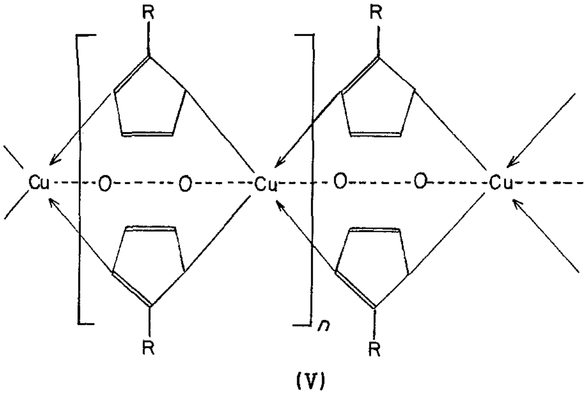
Figure 9 Intensity change of the band at 2925 cm^{-1} plotted against additional heating temperature for 15 min.

methylene blue in solution [62–64]. This system is quite different from the present system, even though a similar process might occur. We must take into consideration the catalytic effect of copper. At already mentioned, the oxidation of propylene proceeds via the formation of an allylic intermediate, possibly allylperoxide or allyl hydroperoxide [45, 46]. The oxygen incorporated into the molecule is probably lattice oxide or gas-phase or adsorbed oxygen. A similar process might occur between the C^4–C^5 double bond (see Structure IV).



(IV)

Similar hydroperoxide formations during the initial stage of oxidation is also observed at the interface between copper or copper oxide and polyolefins [50]. Allara and Chan [51] suggested that the most possible initiation of oxidation involves the decomposition of hydroperoxide to free radicals. They compared the catalytic effects of copper powder, Cu_2O and CuO, and the highest reactivities were obtained with cuprous oxide and a copper surface exposed to air at ambient temperatures. These oxidation processes are carried out at the interface of the film and substrate. However, there is another possibility for explaining the incorporation of oxygen into the imidazole molecule, because some copper complexes can form peroxide with copper [65, 66] and oxidation might be caused by copper within the complex. Ochiai [4] isolated a Cu(II) compound which contains one peroxide group and one bidentate acetate group per copper atoms. Also several papers are available concerning the molecular structure of oxygen-carrying protein [67–69]. Freedman *et al.* [67] identified bound oxygen as O_2^-, and the oxidation states of copper as Cu(II) in hemocyanine. Therefore, in the early stage of oxidation, formation of peroxide in the imadazole copper complex may be possible. The molecular structure of this compound is postulated as shown in Structure V. The valence state of copper in the



(V)

film is not yet elucidated. The molecular structure of imidazolate copper (I) complex is not reported except in Sigwart's work. Sigwart and co-workers [70, 71] reported synthesis of imidazolat copper

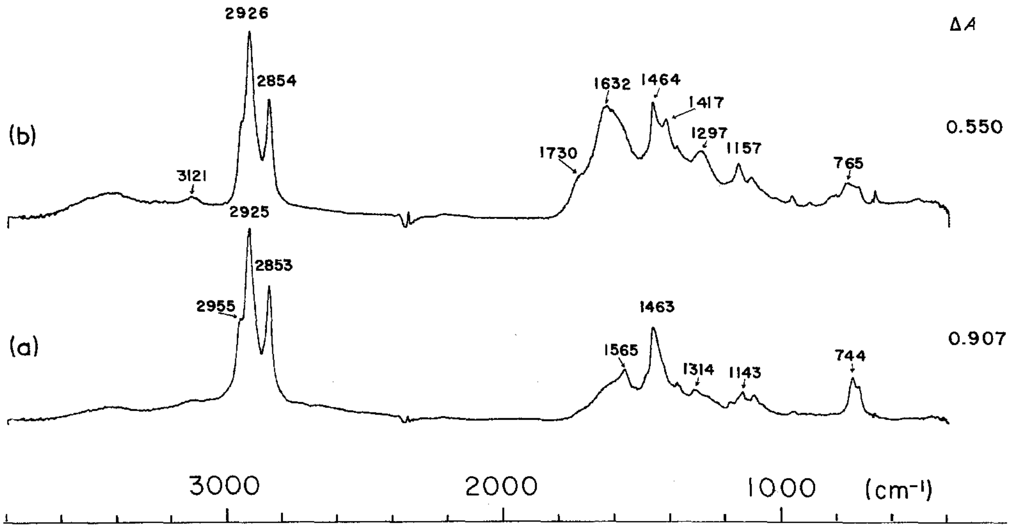
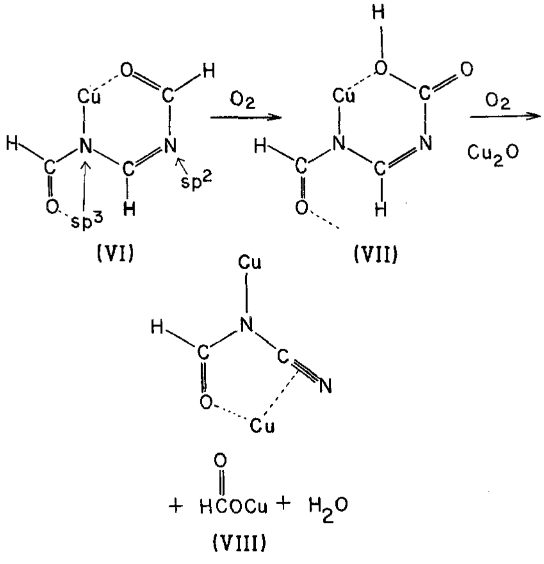


Figure 10 Transmission infrared spectra of: (a) di-undecylimidazolat copper II; and (b) mixture of di-undecylimidazolat copper II and copper (1:3 in weight ratio) after heating at 150° C for 4.5 h.

(I) in acetonitrile but a detailed study of molecular structure has not yet been made. Tompkins and co-workers [20, 21] have found that the oxidation state of copper in the benzimidazole film on the copper substrate is cuprous (Cu(I)) using XPS, whereas the mole ratio of undecylimidazole and copper on the surface is known to be 2:1 [58]. A further study is required to solve this problem. We tentatively assume that the valence state of copper in the film which is exposed to air for a considerably long time is cupric (Cu(II)).

3.3. Thermal stability of diundecylimidazolat copper (II)

In order to understand the catalytic effect of the substrate, a 1:3 weight ratio of di-undecylimidazolat copper II complex and copper powder was mixed and heated at 150° C for 4.5 h and compared with the heat-treatment of di-undecylimidazole copper II without copper. Figs. 10a and b indicate the KBr transmission spectra of the complex without and with copper, respectively. Spectrum B clearly shows a more progressed oxidation state, indicating the catalytic effect of copper. The progress of oxidation is also observed, though to a lesser extent, in spectrum A because of the appearance of the carbonyl related band in the 1750 to 1200 cm^{-1} region. When spectrum B in Fig. 10 is compared with the reflection-absorption spectrum such as spectrum C in Fig. 4, some differences are evident. Spectrum B in Fig. 10 shows a higher relative intensity between the CH_2 band in the 3000 to 2800 cm^{-1} region and the carbonyl bands in the 1800 to 1200 region than the spectrum in Fig. 4, indicating a slower elimination rate of the alkyl group from the molecule when the powdered bulk sample is used. This is due to the difference in surface area of the compound in bulk and as a very thin film. Additionally, a relatively intense band is noticeable at 1730 cm^{-1}. This band is considered to be due to the carbonyl band produced by oxidation of the imidazole ring. It is reasonable to think of the oxidation of aldehyde parts as being attached to the two nitrogens, because the catalytic acid is possibly produced. The rising base line observed from 3300 to 2800 cm^{-1} indicates the existence of the hydrogen-bonded OH stretching mode.



The molecular structure shown in (VI) was proposed as the intial degradation compound in our previous paper [24]. On the metal substrate the carboxylic acid group produced can react quickly with the substrate and eventually the elimination of the carboxylate and production of the nitrile take place [24]. Therefore, the initial degradation compound of (VI) is converted quickly to the final compound (VIII). It is postulated that the rate-determining step of the degradation is the reaction speed of carboxylic acid produced as an intermediate compound and metal oxide. This degradation process can explain the difference in the rate of degradation on differently preoxidized surfaces. In the region of 1800 to 1200 cm^{-1} of spectrum C in Fig. 6, a carbonyl band is observed around 1730 cm^{-1}, whereas no band is observed at this location in the corresponding spectra in Figs. 4 and 5. This indicates the low reactivity of the intermediate compound with CuO.

3.4. Thermal stability of the complex in vacuum

Fig. 11a shows the result of heating a copper substrate in vacuum at 150° C for 15 min after depositing a 50 nm thick undecylimidazole film. It was cooled slowly in the vacuum oven, which required approximately 50 min to be cooled to 60° C. Fig. 11b shows the spectrum after heating the 150 nm thick undecylimidazole film at 170° C for 2 h in vacuum. This time it took approximately 2 h to cool to 60° C in vacuum.

Fig. 11a does not show any noticeable change in the spectrum after heat-treatment. Fig. 11b shows an increase in the band around 1590 cm^{-1}, which is probably caused by the residual air in the vacuum oven. Nevertheless, the spectra changes are very small compared with that for the specimen heat-treated in air. The reduction of the CH_2 band at 2925 cm^{-1} due to heating in vacuum was 20% at 150° C for 15 min, and 72% at 170° C for 2 h. The reduction of this band is due to the simple evaporation of undecylimidazole from the surface [55] rather than the degradation of the imidazole molecule, because the residual undecylimidazole complex on copper did not show any significant spectral changes. In contrast to the evaporation phenomenon described here (Fig. 8), the degradation process produces carbonyl bands on the copper surface and the degradation compound is not volatile.

It is interesting to notice that the complex is oxidized from the surface very quickly when the copper substrate with the imidazole film is removed from the vacuum oven at relatively high temperature. The surface colour changes to brown very quickly and the surface degradation compound is easily removed by water. These results indicate that molecular oxygen is necessary for

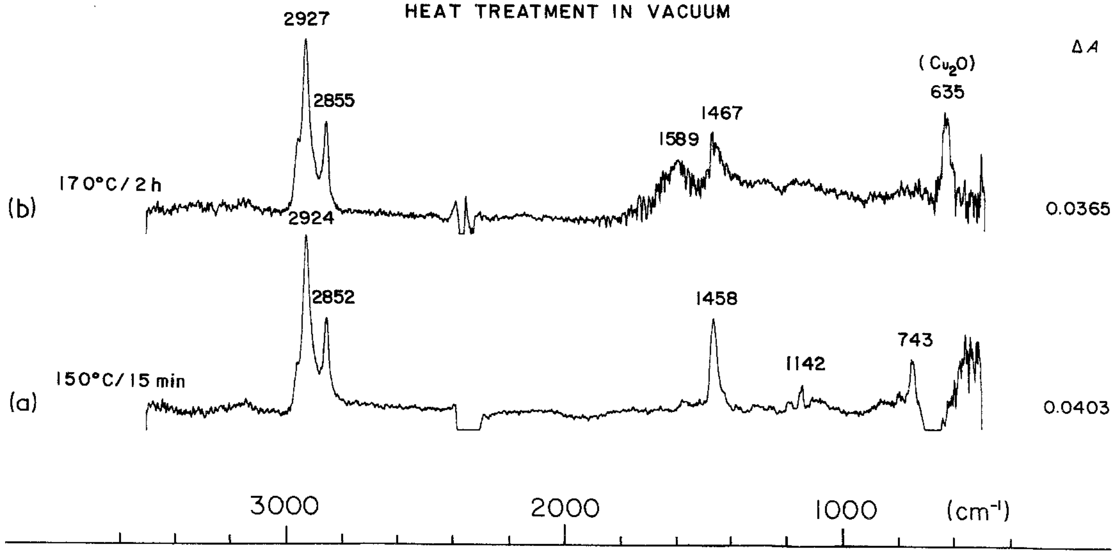


Figure 11 Reflection-absorption infrared spectra of: (a) 50 nm thick undecylimidazole on copper after heating in vacuum at 150° C for 30 min; and (b) 150 nm thick undecylimidazole on copper after heating in vacuum at 170° C for 2 h.

degradation and that it takes place initially on the film surface rather than the interface between the film and substrate. This is supported by the depth profile of the film [55], where a further degraded structure was observed at the outermost layers.

4. Conclusion

Undecylimidazole complex on copper oxide exhibited different morphology and orientation depending on the preoxidation condition of the copper substrate. The complex on the non-preoxidized substrate showed an amorphous structure and random orientation, whereas a randomly oriented semicrystalline complex was observed on the substrate preoxidized at 150° C for 30 min. The orientation of undecylimidazole on the substrate preoxidized at 230° C for 30 min showed a nearly perfect orientation of the imidazole ring. These differences are attributed to the reactivity of undecylimidazole with the substrate surface. The faster reaction rate of Cu_2O and undecylimidazole compared to the deposition rate of undecylimidazole and evaporation rate of the solvent provide a semicrystalline structure, compared to the amorphous structure produced by the slower reaction rate of copper and undecylimidazole. The very low reactivity of CuO and undecylimidazole produces flat orientation of the imidazole ring.

The rate of degradation of the complex also depends on the preoxidation condition. The rate of degradation was in the order non-preoxidized > preoxidized (150° C for 30 min) > preoxidized (230° C for 30 min). Two kinds of copper were postulated as the oxidation catalyst: copper at the interface and in the film. Di-undecylimidazolat copper II, without the addition of copper, shows degradation probably by the catalytic effect of copper in the film. However, the addition of copper into the complex enhanced the rate of degradation. The appearance of carboxylic acid groups suggested an intermediate state of degradation. The reactivity of the carboxylic acid group and the substrate surface is postulated to be the rate-determining step of the degradation. Molecular oxygen is necessary for the degradation which takes place from the outer layer of the film, probably catalysed by the copper in the film at the initial stage of degradation.

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References

1. J. B. COTTON, Proceedings 2nd International Congress on Metallic Corrosion, NACE, New York (1963) p. 590.
2. I. DUGDALE and J. B. COTTON, *Corros. Sci.* **3** (1963) 69.
3. J. B. COTTON and I. R. SCHOLES, *Brit. Corros. J.* **2** (1967) 1.
4. R. WALKER, *Anti-Corrosion* **17** (1970) 9.
5. F. MANSFELD, T. SMITH and E. P. PERRY, *Corrosion* **27** (1971) 289.
6. S. M. MAYANNA and T. H. V. SETTY, *Corros. Sci.* **15** (1975) 625.
7. G. W. POLING, INCRA Project No. 185, February (1979).
8. N. K. PATEL, J. FRANCO and I. S. PATEL, *J. Ind. Chem. Soc.* **54** (1977) 815.
9. G. N. EKILIK, V. P. GRIGOREV and V. V. EKILIK, *Zashch. Met.* **14** (1978) 357.
10. H. USHIYAMA, Y. KAJIYAMA and T. YOSHIOKA, *Jap. Kokai Tokkyo Koho* **79** (1979) 72, 223.
11. A. SAITO, H. TASHIRO and S. ANO, *ibid.* **79** (1979) 148, 148.
12. Nippon Steel Corp. *ibid.* **81** (1981) 113, 381.
13. G. W. POLING, *Corros. Sci.* **10** (1970) 359.
14. N. MORITO and W. SUETAKA, *Nippon Kinzoku Gakkaishi* **35** (1971) 1165.
15. N. G. KLYUCHNIKOV, V. F. USHENINA and I. A. BARABASH, *Uch. Zap. Mosk. Gos. Pedagog. Inst.* **340** (1971) 278.
16. R. F. ROBERTS, *J. Electron Spectrosc. Relat. Phenom.* **4** (1974) 273.
17. D. CHADWICK and T. HASHIMI, *Corros. Sci.* **18** (1979) 457.
18. P. G. FOX, G. LEWIS and P. J. BODEN, *ibid.* **19** (1979) 457.
19. N. D. HOBBINS and R. F. ROBERTS, *Surf. Technol.* **9** (1979) 235.
20. H. G. TOMPKINS and S. P. SHARMA, *Surf. Interface Anal.* **4** (1982) 261.
21. H. G. TOMPKINS, D. L. ALLARA and G. A. PASTEUR, *ibid.*
22. S. YOSHIDA and H. ISHIDA, *J. Chem. Phys.* **78** (1983) 6960.
23. *Idem*, *J. Adhes.* in press.
24. *Idem*, *Surf. Sci.* submitted.
25. Shikoku Chemicals Technical Report, "Glicoat T and L" (1979).
26. I. C. G. OGLE and G. W. POLING, *Canad. Met. Q.* **14** (1975) 37.
27. D. C. FROST, A. ISHITANI and C. A, McDOWELL, *Mol. Phys.* **24** (1972) 861.
28. T. ROBERT and G. OBBERGELD, *Phys. Status Solidi (a)* **14** (1972) 277.
29. F. COTTON and G. WILKINSON, "Advanced Inorganic Chemistry" (Wiley, New York, 1980) p. 801.
30. T. NOTOYAMA and G. W. POLING, *Corrosion* **32**

(1976) 216.

31. J. A. J. JARVIS and F. A. WELL, *Acta Crystallogr.* **13** (1960) 1027.
32. F. MANSFELD and T. SMITH, *Corrosion* **29** (1973) 105.
33. I. B. JOHN, *J. C. Eng. Data* **7** (1962) 277.
34. Y. MOROOKA, Y. MARIKAWA and A. OZAKI, *J. Catal.* **7** (1967) 23.
35. R. S. MANN and K. C. YAO, *Int. Eng. Chem. Prod. Res. Develop.* **10** (1971) 25.
36. O. N. KIMKHAI, V. V. POPOVSKII, G. K. BORESKOV, T. V. ANDRUSHKEVICH and T. B. DNEPROVSKAYA, *Kinet. Katal.* **16** (1975) 96.
37. A. G. ANSHITS, V. D. SOKOLOVSKII, G. K. BARESKOV, A. A. DAVYDOV, A. A. BUDNEVA, V. I. ANDEEV and I. I. ZAKHAROV, *ibid.* **16** (1975) 95.
38. Y. B. GOROCHOVATSKII, *Z. Chem.* **16** (1976) 41.
39. D. N. RUNDELL, H. M. SALTSBURG and W. D. SMITH, *Chem. Eng. Sci.* **35** (1980) 1113.
40. A. G. ANSHITS, V. D. SOKOLOVSKI, G. K. BORESKOV and A. A. PANYDOV, *Kinet. Katal.* **19** (1978) 366.
41. *Idem, ibid.* **19** (1978) 372.
42. M. AKIMOTO, H. TSUNEKI and E. ECHIGOYA, *Nippon Kagaku Kaishi* **805** (1978).
43. L. D. KRENZKE, G. W. KEULKS, A. V. SKLYAROV, A. A. FIRSOVA, M. Yu. KUTIREV, L. Ya. MARGOLIS and O. V. KRYLOV, *J. Catal.* **52** (1978) 418.
44. G. KREMENIC, *Simp. Iberoam, Catal.* **7** (1980) 581.
45. D. J. HUCKNALL, "Selective Oxidation of Hydrocarbons" (Academic Press, New York, 1974) Ch. 3, p. 23.
46. C. DANIEL and G. W. KEULKS, *J. Catal.* **24** (1972) 529.
47. R. H. HANSEN, C. A. RUSSELL, T. DEBENEDICTIS, W. M. MARTIN and J. V. PASCALE, *J. Polym. Sci.* A-2 (1964) 587.
48. R. H. HANSEN, T. DEBENEDICTS and W. M. MARTIN, *Polym. Eng. Sci.* **5** (1965) 223.
49. M. G. CHAN and D. L. ALLARA, *ibid.* **14** (1974) 12.
50. L. REICH and S. S. STIVOLA, "Autoxidation of Hydrocarbons and Polyolefins" (Dekker, New York, 1069) Ch. 4.
51. D. L. ALLARA and M. G. CHAN, *J. Polym. Sci. Polym. Chem. Ed.* **14** (1976) 1857.
52. F. J. BOERIO and L. ARMOGAN, *Appl. Spectrosc.* **32** (1978) 509.
53. G. W. POLING, *J. Electrochem. Soc.* **116** (1969) 958.
54. H. ISHIDA, H. SONODA, K. NAGASAWAWA and K. ISHIDA, "15th Applied Spectroscopy in Tokyo", preprint (1979).
55. S. YOSHIDA and H. ISHIDA, to be published.
56. M. GOODGAME and F. A. COTTON, *J. Amer. Chem. Soc.* **84** (1962) 1543.
57. C. W. BUNN, *Trans. Faraday Soc.* **35** (1939) 482.
58. S. MATSUBARA and T. MINAGAWA, Shikoku Chemicals Inc., private communication (1978).
59. S. A. FRANCIS and A. H. ELLISON, *J. Opt. Soc. Amer.* **49** (1959) 131.
60. R. G. GREENLER, *J. Chem. Phys.* **44** (1966) 310.
61. J. A. ALLEN, *Trans. Faraday Soc.* **48** (1952) 273.
62. E. H. WHITE and M. J. C. HARDING, *J. Amer. Chem. Soc.* **84** (1964) 5686.
63. G. RIO and B. SERKIN, *J. Chem. Soc. Chem. Commun.* (1975) 849.
64. H. S. RYANG and C. S. FOOTE, *J. Amer. Chem. Soc.* **101** (1979) 6693.
65. A. J. MELVEGER, L. R. ANDERSON, C. T. RATCLIFFE and W. B. FOX, *Appl. Spectrosc.* **26** (1972) 381.
66. E. OCHIAI, *Inorg. Nucl. Chem. Lett.* **9** (1973) 987.
67. T. B. FREEDMAN, J. S. LOHR and T. M. LOHR, *J. Amer. Chem. Soc.* **98** (1976) 2809.
68. J. A. LARRABEE, T. G. SPIRO, N. S. FERRIS, W. H. WOODRUFF, W. A. MALTESE and M. S. KERR, *ibid.* **99** (1977) 1979.
69. S. SALAMA and T. G. SPRIO, *ibid.* **100** (1978) 1105.
70. P. HEMMERICH and C. SIGWART, *Experientia* **19** (1963) 488.
71. C. SIGWART, P. KRONECK and P. HEMMERICH, *Helv. Chem. Acta* **53** (1970) 177.
72. I. E. WACHS and R. J. MADIX, *Surf. Sci.* **84** (1979) 375.
73. J. T. YATES and R. R. CAVANAGH, *J. Catal.* **74** (1982) 97.
74. R. P. GROFF and W. H. MANOGUE, *ibid.* **79** (1983) 462.

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