obtained at 0.005 M for compounds (I) and (II). While for compound (III) the minimum (Icorr.) is obtained at 0.0025 M; whereas for compound (IV) it is obtained at 0.004 M.

2.2.1.4. Behavior of the pre-treated copper electrode in air prior to immersion in the natural water-free additive:

Figure (7) represents the cathodic and anodic polarization measurments, carried out after keeping the copper electrode exposed to air for various period of time (namely: 1, 8, 12, 20 and 24 hrs.) as a pre-treatment prior to immersion of the electrode in natural water free additives.

The results of Figure (7) reveals that the pre-exposure period of copper electrodes in air has a significant effect on both the cathodic and anodic polarization curves. The experimentally determined values of the electrochemical parameters (i.e. E_{corr}, I_{corr} and Bc) are given in Table (9). These data indicate that values of E_{corr} are approximately the same independent on the pre-exposure time of the copper substrate in air. Also, it is observed that the values of I_{corr} increase with increasing the pre-exposure time of copper in air. In the mean time, the values of Bc (i.e. cathodic Tafel slope) decrease.

2.2.2. Behavior of the copper electrodes exposed to air for various periods of time as a pre-treatment prior to immersion in natural water containing additives:

Figures (8-11) represents the cathodic and anodic polarization curves, carried out by keeping the copper electrode exposed to air for various periods of time (namely: 1, 8, 12, 20 and 24 hrs.) as a pre-treatment prior to immersion of the copper electrode in the test solution (namely: natural water containing (0.005,0.005,0.0025 and 0.004M) of compounds I, II, III and IV, respectively. In these Figures (8-11), the cathodic and anodic polarization curves recorded without keeping the copper electrode exposed to air prior measurements the same test solutions is included as the reference curve for comparison proposes. The results of Figures (8-11) reveal that the pre-exposure priod of copper electrode in air has a significant effect on the cathodic and anodic polarization measurements. Clearly, increasing the pre-exposure time of copper electrode in air prior to immersion of copper electrode in the natural water containing (0.005M) from compound (I) (Figure 8) lead to shifting the cathodic and anodic current density to a lower value until a minimum is reached at 12 hours after which it becomes nearly constant.

In presence of compounds II, III, or IV (Figures 9-11) the cathodic and anodic polarization curves are shifted towards lower current density. Such shift attains its minimum at 12 hours pre-exposure time of the copper electrode in air. Increasing the pre-exposure time of copper electrodes in air for a time longer than 12 hours lead to shifting the cathodic and anodic polarization curves towards higher current densities as compared with that obtaind in case of 12 hours pre-exposure time.

The electrochemical parameters such as, corrosion potential (E_{corr}), corrosion current density (I_{corr}) and the cathodic Tafel slope (Bc) obtained from the curves of Figures (8-11) are given in Tables (10-13). These data indicate that increasing the pre-exposure time of copper in air lead to shifting the corrosion potential (E_{corr}) to amore negative values until a maximum is reached at about 12 hours after which it reverses its direction to a decrease in the potential but still in the negative region. Also, these data indicate that the value of (I_{corr}) obtained in case of blank (i.e. zero exposure time in air) was found to decrease with the increase of the pre-exposure time of copper in air until a minimum is reached at about 12 hours. On the other hand, the value of the cathodic Tafel slope (Bc) is found to increase also with the increase of the pre-exposure time of copper in air and a maximum value of (Bc) is obtained at about 12 hours.

2.2.3. Effect of Immersion Time in the Test Solutions:

Figures (12-15) show the cathodic and anodic polarization curves of copper electrodes after different immersion times at the open circuit potential in natural water containing 0.005,0.005,0.0025 and 0.004 M from compounds I, II, III and IV, respectively. In these Figures (12-15), the cathodic and anodic poloarization curves recorded for 1 hr immersion in the test solutions containing each compound is included as the reference curves for comparison purpose.

Inspection of the curves of these Figures reveals that, the cathodic and anodic polarization curves are influenced with immersion time at the open circuit potential. Clearly, these curves indicate that in presence of compound (I) (Figure 12), compound (II) (Figure 13) and compound (IV) (Figure 15) the cathodic and anodic polarization curves are shifted to a lower current densities with immersion time at the open circuit potential.

Such shift attains its minimum after 12 hr immersion in the investigated time scale. For immersion time higher than 12 hr, the current densities of the cathodic and anodic polarization curves are shifted to a higher values as compared with that recorded for the reference curves.

On the other hand, in presence of compound III, the cathodic and anodic polarization curves (Figure 14) are shifted to a lower current densities and such shift attains its minimum after 12 hr immersion in the investigated time scale. For immersion time higher than 12 hr practically no further change in the current densities was noticed from both the cathodic and anodic polarization curves.

The values of corrosion potentials (E_{corr}), corrosion current densities (I_{corr}) and the cathodic Tafel slopes (Bc) are calculated from the cathodic polarization curves of Figures (12-15) and listed in Tables (14-17). According to these data it is illustrated that the values of these parameters are greatelly influenced with immersion time in the test solutions at the open circuit potentials. Appearntly, the E_{corr} is shifted to more negative values, the I_{corr} is decreased and a significant increase in the (Bc) were observed depending on the time of immersion.

2.3. Discussion:

When copper is immersed in water, some oxide layer of copper may form very slowly and coat the bar metal surface. These oxides coating, even if extremely thin, could form a partial barrier to continued attack, and slow down the rate of corrosion almost to a standstill.

A surface layer formation, whether it is oxide or any other compound is a major factor in corrosion resistance, particularly if the layer effectively separates the underlying metal from its environment. Such a naturally formed coating must be diffusion resistant to be effective.

2.3.1. Behavior in the natural water:

The curves shown in Figure (2) indicate that in case of natural water-free additive, the cathodic process taking place on the copper electrode is a chemical activation and concentration polarization. Apparently, each curve is characterized by two consequence limiting currents. This would indicate that the reduction of oxygen is by far the major cathodic process, which takes place via hydrogen peroxide. Consequently, it is suggested that the reduction of oxygen can be expressed by consecutive two electron steps involving a reduction to hydrogen peroxide (H_2O_2) first (***Kaesche, 1985***):

$$O_2 + 2\,H_2O + 2e^- = H_2O_2 + 2OH^- \qquad (5)$$

followed by a further reduction:

$$H_2O_2 + 2OH^- + 2e^- = 4OH^- \qquad (6)$$

It was reported that ***(Jinturkar et al., 1998)*** oxygen has a marked effect on the corrosion of copper in many aqueous solutions. In near-neutral solution, the cathodic partial reaction is oxygen reduction