CUMINUM CYMINUM (Jeeru) seeds extract a green corrosion inhibitor for brass in HNO_3 media.

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Abstract : *Cuminum cyminum* (Jeeru) seeds extract studied for its inhibitory effect on corrosion of brass in different concentration of HNO_3 solution using weight loss method, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The inhibition efficiency increases with increase in extract concentration but decreases with increase in temperature. The temperature study on corrosion behaviour in temperature range 313-333K at 0.1 M nitric acid. The value of Free energy of adsorption (ΔG^0_{ads}), Heat of adsorption (Q_{ads}), Energy of Activation (E_a), Enthalpy of adsorption (ΔH^0_{ads}) and Entropy of adsorption (ΔS^0_{ads}) were calculated. Adsorption studies revealed that Langmuir adsorption isotherm is the best adsorption model applicable to the adsorption of *cuminum cyminum* extract on brass surface. Present study indicates that *cuminum cyminum* seeds extract is a good inhibitor for the corrosion of brass in nitric acid medium.

***IndexTerms* - Corrosion, Cuminum cyminum, Langmuir, Nitric acid, Potentiodynamic polarization, Electrochemical impedance spectroscopy.**

I. INTRODUCTION

Corrosion is a natural process commonly defined as the deterioration of a metal or its properties because of a reaction with its environment. Corrosion can cause dangerous and expensive damage to petrochemical industries, bridges and public buildings etc. The cost of this phenomenon is very costly with 4 % of the Gross Domestic Product (GDP) of industrial countries [1-2].

Brass is broadly used as tubing material for condensers and heat exchangers in various cooling water systems [3-4]. Copper and its alloys are widely used in industry especially in heating and cooling system because of their excellent electrical and thermal conductivity [5]. This family of copper alloys is susceptible to a corrosion process known as dezincification and it susceptibly increases as zinc content increases [6].

Jeera seeds are used in the cuisines of many different cultures, in both whole and ground form. It helps to add an earthy and warming feeling to cooking; making it a staple in certain stews and soups, as well as curries and chili [7, 8]. The main phytoconstituent of Jeera seeds is cuminaldehyde. It is likely to impart good corrosion inhibition activity due to presence of aromatic ring, aldehyde and isopropyl groups as substituents. Survey of literature reveals that no work has been done on Jeera extract as corrosion inhibitors.

II. MATERIALS AND METHODS

1. Preparation of sample and solution: The brass metal used in this study with a chemical composition 60.73% Cu, 39.21% Zn, 0.01% Fe, 0.02% Sn and 0.04% Pb. The brass specimens of the size 4.4 x 2.0 x 0.181 cm were used. The specimens were cleaned by washing with distilled water, degreased by acetone, washed once more with doubled distilled water and finally dried and weighted by using electronic balance. The corrosive solution was prepared by diluting analytical grade of HNO_3 purchased from Merck using double distilled water.

2. Preparation of extract: Stock solutions of Jeera (*Cuminum cyminum*) dried seed powder (10 g) was soaked in double distilled water (500 ml) and refluxed for 5 h. The aqueous solution was filtered and concentrated to 100 ml. This extract was used to study the corrosion inhibition properties [9].

3. Weight loss measurements: For weight-loss measurement, the brass specimen having an area of approximately 0.206 dm^2 were each completely suspended in 230 ml of HNO_3 solution with and without different Jeera seed extract concentrations using glass hooks at 301± 1 K for 24 h. The coupons were retrieved after 24 h, washed with distilled water, dried well and reweighed. From the weight loss data, corrosion rate (CR) was calculated.

4. Temperature effect: To study temperature effect, brass coupons were completely immersed in 230 ml of 0.1 M HNO_3 solution with and without different Jeera seeds extract concentrations using glass hooks and corrosion rate were determined at 313, 323 and 333 K for 2 h to calculate inhibition efficiency (I.E.), activation energy (E_a) and heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG^0_{ads}).

5. Potentiodynamic polarization measurements: Both the potentiodynamic and EIS measurement are carried out using CHI608C –series, U.S. Model with CH- instrument. For polarization study, metal specimens were immersed with and without *Cuminum cyminum* extract in 0.1 M HNO_3 solution. In the electrochemical cell brass specimens having an area of 1 cm^2 was used as a working electrode , Ag/AgCl electrode as a reference electrode and platinum electrode as an auxiliary electrode and allowed to establish a steady-state open circuit potential (OCP) for approximately 15 min. The polarization curves were plotted with current Vs potential. An anodic and cathodic polarization curve gives corresponding anodic and cathodic Tafel lines. The intersect point of Tafel lines gives the corrosion potential (E_{corr}) and corrosion current (i_{corr}) [10].

6. Electrochemical Impedance Spectroscopy (EIS) measurements: EIS measurements were made at corrosion potentials over a frequency range of 0.1 to 10^5 Hz by a sine wave with potential perturbation amplitude of 5 mV. The real Z' and imaginary -Z'' parts were measured at various frequencies. From the plot of Z' Vs -Z'', the charge transfer resistance (R_{ct}), and double layer capacitance (C_{dl}) were calculated. An experiment was carried out in absence and presence of inhibitor.

III. RESULTS AND DISCUSSION

1. Weight loss experiments: The weight loss experiments was carried out in 0.1, 0.25, 0.5 and 1.0 M HNO_3 solution containing 600, 800, 1000, 1200 ppm concentration of *Cuminum cyminum* at 301±1 K for an exposure period of 24 h was investigated. Inhibition efficiency (I.E.) was calculated by using following equation,

$$\text{I.E. } (\%) = \left\{\frac{(W_u - W_i)}{W_u}\right\} \times 100 \qquad (1)$$

Where: Wu - Weight loss in absence of inhibitor, Wi - Weight loss in presence of inhibitor.

The surface coverage (θ) of the brass specimen for different inhibitor concentration in HNO_3 solution have been evaluated by weight loss experiments using the following equation,

$$\theta = \frac{(W_u - W_i)}{W_i} \qquad (2)$$

As the acid concentration increases corrosion rate increase while I.E. decreases. At constant acid concentration, as the inhibitor concentration increases corrosion rate decreases while I.E. increases (Table-1 and Figure-1).

Table 1: Effect of HNO_3 concentration on corrosion rate (CR) and inhibition efficiency (IE) of brass having different concentration of *Cuminum cyminum* seed extract.

Inhibitior concen tration (ppm)	Acid concentration					
	0.1 M		0.25 M		0.5 M	
	CR (mg /dm²d)	I.E. (%)	CR (mg/dm²d)	I.E. (%)	CR (mg/dm²d)	I.E. (%)
Blank	1820.39	-	9393.20	-	15902.91	-
600	163.11	91.04	3577.67	61.91	8587.38	46
800	138.83	92.37	2703.88	71.21	6825.24	57.08
1000	93.98	94.84	2213.59	76.43	5451.46	65.72
1200	49.13	97.30	1878.64	80.00	4902.91	69.17

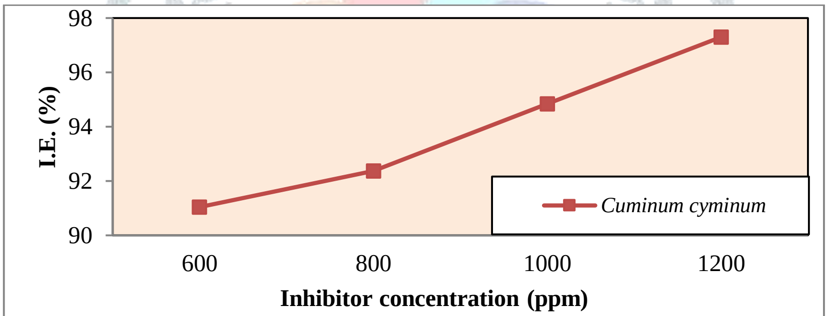

Fig.1: Effect of inhibitor concentration on inhibition efficiency (IE) for brass in 0.1 M HNO_3 at 301±1K, 24h.

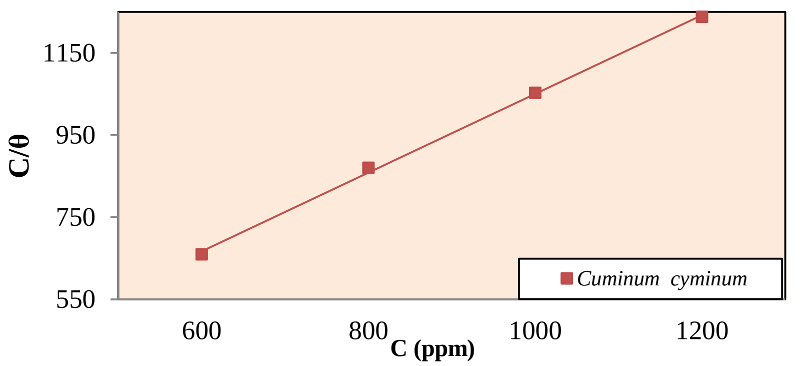

Fig. 2 : Langmuir adsorption isotherm plot of C/θ versus 'C' for brass in 0.1 M HNO_3 containing *Cuminum cyminum* as green inhibitor at 301 K.

The surface coverage 'θ' value was calculated by using equa.-2. The plot of inhibitor concentration C_{inh} versus C_{inh}/θ is presented in Fig. 2 which gives straight line with almost unit slope indicates that the system follows Langmuir Adsorption isotherm [11]. This isotherm can be represented as,

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (3)$$

Where, K_{ads} is the equilibrium constant and C_{inh} is the inhibitor concentration. Linear plot obtained from Fig. 2 shows that constituents of *Cuminum cyminum* extract on a brass surface making a barrier for charge and mass transfer between the metal and environment follows Langmuir adsorption isotherm which shows inhibition efficiency.

2. Temperature effect: The mass loss experiments were also carried out at different temperature 313, 323 and 333 K in 0.1M HNO_3 to investigate the influence of temperature on the rate of corrosion for immersion period of 2h.The value of energy of activation (E_a) has been calculated with the help of Arrhenius equation [11].

$$\log\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (4)$$

Where, ρ_1 and ρ_2 are the corrosion rate at temperature T_1 and T_2 respectively. The values of heat of adsorption (Q_{ads}) were calculated by following equation [12].

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right]\left[\frac{T_1T_2}{T_2-T_1}\right] \qquad (5)$$

Where, θ_1 and θ_2 ($\theta = W_u - W_i / W_u$) are the fraction of the metal surface covered by the inhibitor at temperature T_1 and T_2 respectively. The negative and lower values of Q_{ads} support higher I.E. achieved by spontaneous adsorption of the inhibitor.

Table-2: Temperature effect on corrosion rate (CR) (log ρ) for brass in 0.1M HNO_3 in absence and presence of *Cuminum cyminum* extract for an immersion period of 2h.

Inhibitor	**Inhibitor concentration (ppm)**	**Temperature**		
		313 K	**323 K**	**333 K**
		CR (log ρ)	**CR (log ρ)**	**CR (log ρ)**
Blank	-	3.35	3.54	3.67
***Cuminum cyminum* (Jeeru)**	**600 ppm**	2.88	3.20	3.36
	800 ppm	2.72	3.07	3.24
	1000 ppm	2.61	2.91	3.18
	1200 ppm	2.54	2.81	3.04

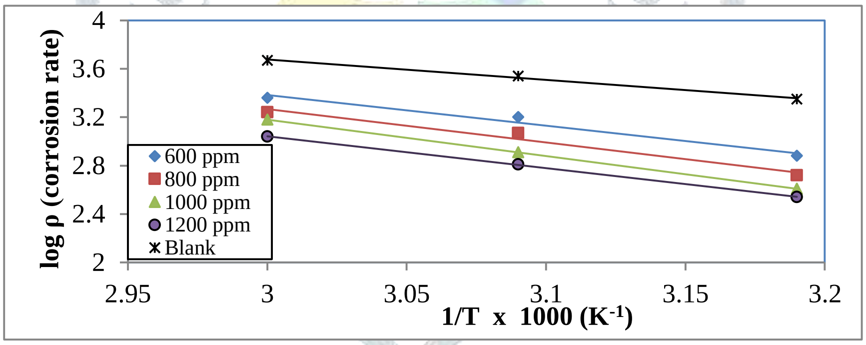

Fig.3: Arrhenius plots for brass in 0.1 M HNO_3 in absence and presence of the different concentration of *Cuminum cyminum* extract.

3. Potentiodynamic polarization study: Figure-4 represents the potentiodynamic polarization curves of brass in 0.1 M HNO_3 in absence and presence of *Cuminum cyminum* seed extract. Electrochemical parameters such as corrosion potential (E_{corr}),corrosion current density (i_{corr}), anodic Tafel slope (βa), cathodic Tafel slope (βc) and percentage inhibition efficiency (I.E.) are given in Table-3.

From Fig. 4 and Table-3, it was observed that the addition of *Cuminum cyminum* extract in acid solution indicates the significant decrease in corrosion current density (i_{corr}) and decrease in the corrosion rate with respect to blank. There is significant change in the anodic and cathodic slopes after the addition of the inhibitor.

Table -3: Potentiodynamic polarization data and Inhibition efficiency (I.E.) of *Cuminum cyminum* extract as green inhibitor for brass in 0.1 M HNO_3.

System	**E_{corr} (mV)**	**I_{corr} (μA / cm^2)**	**Tafel slope (mV / decade)**			**IE (%) Calculeted from (methods)**	
			Anodic (+βa)	**Cathodic (-βc)**	**β (mV)**	**Polarization**	**Weight loss**
Blank	-0.03	1408	4.72	5.47	1.10	-	-

Cuminum Cyminum	-0.083	543.1	8.61	1.15	0.44	61.43	92.37

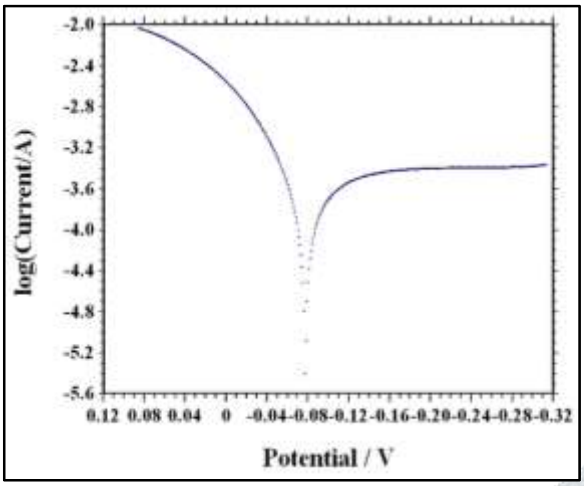

Fig. 4(a): Potentiodynamic polarization curve for brass in 0.1 M HNO_3

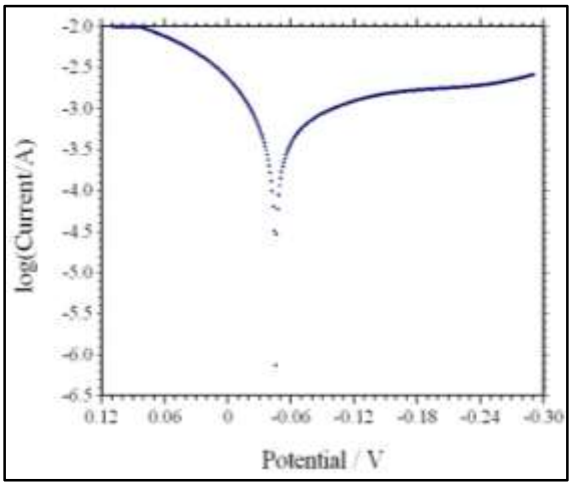

Fig. 4 (b): Potentiodynamic polarization curve for brass in 0.1 M HNO_3 in presence of 800 ppm *Cuminum cyminum* extract.

This Tafel curves indicate that *Cuminum cyminum* function as a mixed type and predominant cathodic inhibitor. Inhibition efficiency (I.E.) from polarization study was calculated using following equation.

$$\text{I.E. } (\%) = \frac{i_{corr(uninh)} - i_{corr(inh)}}{i_{corr(uninh)}} \qquad (6)$$

4. Electrochemical impedance spectroscopy (EIS) measurements: Nyquist plots for the corrosion of brass in 0.1 M HNO_3 solution in absence and presence of Jeeru extract was examined by EIS method at room temperature was shown in Table-4 and in Figure-5.

It is observed from Figure-5 that the impedance diagram is almost semi circular in appearance, but not perfect semicircle. The difference has been attributed to frequency dispersion. The semi circular nature of the plots indicates that the corrosion of brass is mainly controlled by charge transfer process.

The diameter of capacitive loop in the presence of inhibitor is bigger than that in the absence of inhibitor. The high frequency capacitive loop is related to the charge transfer resistance (R_{ct}). To calculate the double layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum was found as presented in the following equation [13].

$$C_{dl} = \frac{1}{2\pi F_{max} R_{ct}} \qquad (7)$$

Where 'f' is the frequency at the maximum height of the semicircle on the imaginary axis and R_{ct} is the charge transfer resistance [14].

Inhibition efficiency (I.E.) from EIS method was calculated using following equation:

$$I.E.(\%) = \frac{Cdl(uninhi.) - Cdl(inhi.)}{Cdl\ (uninhi.)}\ x\ 100 \qquad (8)$$

The addition of inhibitor increase R_{ct} value while decreases in C_{dl} values which is due to the adsorption of inhibitor on the metal surface. The results suggest that the inhibitor acts by the formation of a protective layer on the surface, which modifies the metal/solution interface.The results indicate that C*uminum cyminum* seed extract performs as good inhibitor for the corrosion of brass in nitric acid solution.

Table- 4: EIS parameters for corrosion of brass in 0.1 M HNO_3 containing *Cuminum cyminum* extract.

System	R_{ct} (Ω cm^2)	C_{dl} (μF / cm^2)	IE (%) Calculated from	
			EIS method	Weight loss method
Blank	212.82	6.43	-	-
***Cuminum cyminum* (Jeeru)**	425	0.379	91.24	92.37

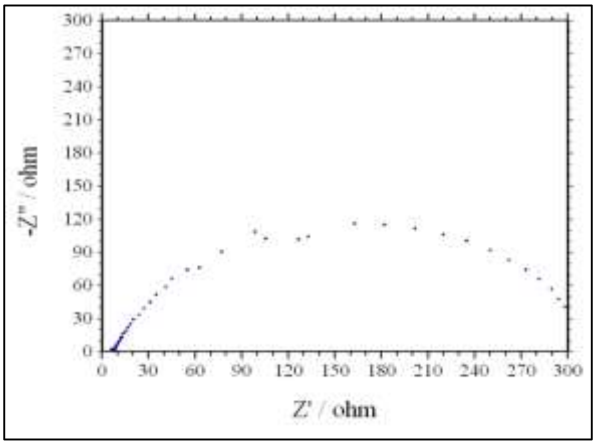

Fig. 5(a): Nyquist plot for brass in 0.1 M HNO_3

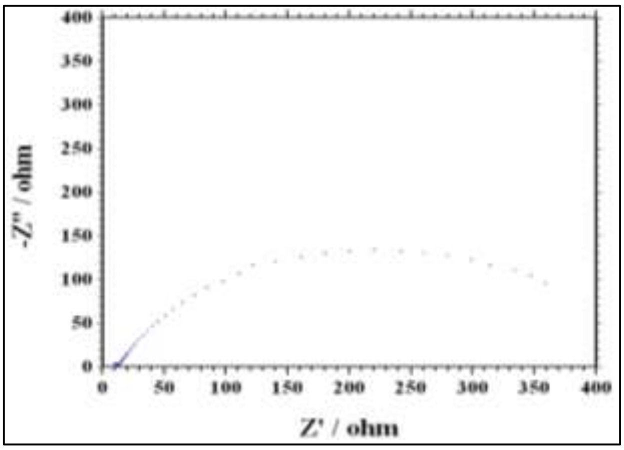

Fig. 5(b): Nyquist plot for brass in 0.1 M HNO_3 in presence of 800 ppm *Cuminum cyminum*

5. Mechanism of corrosion.

The behaviour of anodic dissolution of brass in nitric acid is very complex and consists of dissolution of both zinc and copper. Generally, the anodic reaction for Copper is considered as follows [15-17]:

$Cu \rightarrow Cu(I)_{ads} + e^{-}$ (fast step) (9)
$Cu(I)_{ads} \rightarrow Cu(II) + e^{-}$ (slow step) (10)

Where $Cu(I)_{ads}$ is an adsorbed species onto copper surface and does not diffuse into the bulk solution. Meanwhile, the adsorption of copper ions, Cu (II), on the surface due to its reduction in presence of Zn must be taken into consideration. Also, the anodic dissolution of Zn is considered according to following equation:

$Zn \rightarrow Zn^{2+} + 2e^{-}$ (11)

It should be noticed that the cathodic reaction is not hydrogen evolution reaction at all, because the corrosion potential in all experiments is well above the redox potential of hydrogen evolution in this media. In this way, the predominant mechanism of cathodic reaction has been reported according to the following equation [18]:

$NO_3^{-} + 4H^{+} + 3e^{-} \rightarrow NO + 2H_2O$ (12)

Also, oxygen reduction in acidic media can be considered to be as another cathodic reaction. Based on Eq. (12), the presence of NO_3^{-} ions onto cathodic sites is mandatory for reaction.

6. Mechanism of Inhibition by *Cuminum cyminum* (Jeeru)

Dried cumin contain 2-3 % essential oil, 22 % fatty oil, 18 % protein, 14 free amino acids, flavonoids, glycosides, tannins, resins and gum. The main constituents of cumin are Cuminaldehyde, p-cymene and terpenoid [19].

The main constituent of cumin extract which contains heteroatom and an aromatic ring in its structure is cuminaldehyde. The active oxygen centre of cuminaldehyde may form complex with the metal cation to retard the dissolution of pure brass in HNO_3 medium. Cuminaldehyde can be protonated in an acid medium, predominantly affecting the oxygen atom present in it. Thus, it forms cations, existing in equilibrium with the corresponding molecular form as shown in Equation:

$[C_{10}H_{12}O] + xH^{+} \rightarrow [C_{10}H_{12+x}O]^{x+}$ (13)

When cuminaldehyde adsorbs on the brass surface, electrostatic interaction takes place by partial transfer of electrons from the polar O-atom and the delocalized π electrons around the benzene ring to the metal surface [20]. Adsorption of Cuminaldehyde in Jeera (*Cuminum Cyminum*) seed extract arises from the donor acceptor interactions between free electron pairs of hetero atoms and π-electrons of multiple bonds, vacant d-orbitals of Cu (brass). In case of adsorption of organic compounds on the metallic surface, planarity of molecules must also be taken in to consideration. The cumin extract act as a mixed type inhibitor for brass in nitric acid. Our results are in good agreement with the results obtained by Ladha et al. [19] in their work on cumin extract as corrosion inhibitor for aluminium in HCl medium

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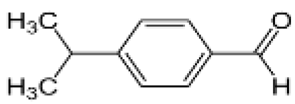
<tr><td>
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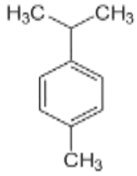
($C_{10}H_{12}O$)</td><td>
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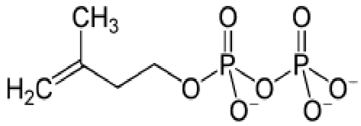
<tr><td colspan="2">
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IV. CONCLUSIONS

From the study the following conclusions can be drawn:

1. As the acid concentration increases the corrosion rate increases.
2. As the inhibitor concentration increase I.E. increases and corrosion rate decreases.
3. *Cuminum cyminum* seed extract adsorbed on metal surface following Langmuir adsorption isotherm.
4. Tafel plost of polarization measurements indicates that the inhibitor behave as a mix type inhibitor.
5. EIS spectra exhibit semi circular in appearance which indicates that the corrosion of brass is mainly controlled by charge transfer process.

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