

BIODEGRADABLE GREEN INHIBITOR (MYRISTICA FRANGANS) AS A CORROSION INHIBITOR OF MILDSTEEL IN 1M HCl

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ABSTRACT

In this investigation attempts have been made to study the inhibitive effect of acid extract of Myristica Frangans (MF) on mild steel in 1M HCl by weight loss, DC Polarization method and AC impedance spectroscopy. Results indicated that MF acts as an effective inhibitor in the acid environment. The inhibition efficiency of MF increased with increase in inhibitor concentration and with temperature. The adsorption of MF follows Langmuir adsorption isotherm. Thermodynamic functions have been evaluated from temperature studies. Electrochemical measurements revealed that MF extract acts as a mixed type inhibitor.

Key words: Myristica Frangans, Mild steel, Acid corrosion inhibitor

INTRODUCTION

Corrosion of metal is a major industrial problem. Corrosion inhibitors are of great practical importance being extensively employed in minimizing metallic waste in engineering materials. There is a wide consideration in literature^[1] regarding the inhibition studies by natural compounds. Extracts of many naturally occurring materials like alkaloids^[2], eucalyptus leaves^[3], tea leaves, pomegranate juice and peels^[4,5] herbal medicinal powder like swertia augustifolia^[6], Datura Metel^[7], Datura Stramonium^[8], Mentha^[8], Mentha Pulgium^[9] were reported to be effective acid corrosion inhibitors. Due to their biodegradability, renewable and eco friendliness, the trend of using such less non

toxic compounds are increasing everyday. The present work is directed to evaluate the extract of *Myristica Frangans* as probable acid corrosion inhibitors for mild steel.

EXPERIMENTAL DETAILS

Extraction of Plant Material

25 grams of dried and powdered MF was refluxed with diethyl ether to remove the lignin and then refluxed with 500 ml of 1M HCl for 3 Hrs. The extract was filtered and made up to 500ml. From this stock solution, different concentrations of the inhibitor (250 ppm to 2000 ppm) were prepared.

Weight loss method

The mild steel specimens were cut in to 5cm x 1 cm coupons for immersion studies and were lacquered so as to expose an area of 1cm² for all electrochemical studies. The specimens were mechanically polished, degreased and dried in acetone, stored in a dessicator and used for all studies. Their edges were abraded with fine grade of emery papers. Chemical composition of mild steel was found to be Carbon 0.126 %, Manganese 0.181 %, Silicon 0.058 % , Phosphorous 0.033%, Sulphur 0.029 %, Chromium 0.012 %, Molybdenum 0.012%, Nickel 0.002% and remaining iron.

Weight loss measurements were carried out in triplicate in the absence and presence of various concentration of the MF extract in 1M HCl for various periods of immersion at room temperature and at different temperatures. From the values, corrosion rate and inhibitor efficiency were calculated.

Electro chemical Measurements

Electrochemical studies were carried out in the absence and presence of extract using conventional three electrode cell with larger area platinum foil as counter electrode, MS as working electrode and saturated calomel electrode (SCE) as reference electrode. Solatron Electrochemical analyzer model (1280B) interfaced with an IBM computer and Z plot and Corrware softwares were used for data acquisition and analysis.

RESULTS AND DISCUSSION

Weight loss method

Effect of Concentration

Corrosion rate of the metal and inhibitor efficiency of the extract obtained by weight loss method for different inhibitor concentrations at various periods of immersion in 1M HCl are depicted in table (1). IE of the inhibitor increases with increase in inhibitor concentration. Maximum efficiency of 90.91% was achieved with 2000 ppm at 24 hours. This behaviour may be attributed to the increase of the surface area covered by the adsorbed molecules of MF with the increase of concentration ^[10]

Table- 1

IE as the function of time of immersion and concentration of MF

Concentration of the inhibitor in ppm	Inhibition Efficiency(%)					
	0.5 hr	1 hr	3 hrs	6hrs	12hrs	24hrs
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250	58.02	62.16	66.42	67.96	77.58	71.98
500	60.92	67.09	72.99	75.81	80.07	78.24
750	66.69	73.28	76.61	78.74	84.29	83.99
1000	69.86	75.5	76.92	82.81	86.95	84.92
1250	71.4	75.98	77.18	83.42	88.09	85.52
1500	74.06	76.97	78.87	83.5	89.92	87.92
2000	74.65	75.39	81.05	85.41	90.74	90.91

Effect of Immersion Time

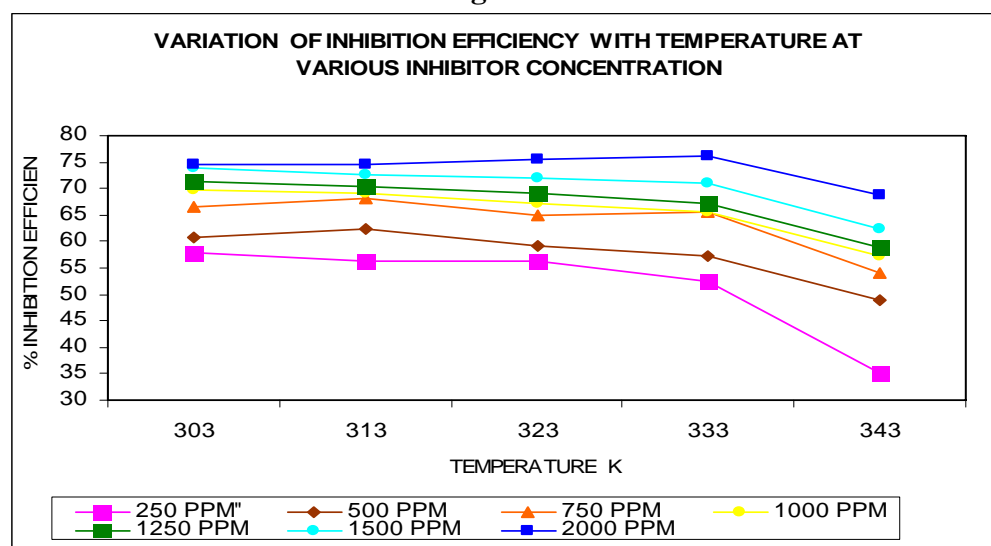
For a given time of immersion, inhibition efficiency increased with the increase in concentration. At all concentrations, IE increased with immersion time. A maximum efficiency of 90.91% was obtained at 24 hours.

This increase of IE with respect to time of immersion indicates the stability of adsorbed layer on the metal surface ^[11]

Effect of Temperature

Temperature studies were carried out in the absence and presence of varying concentration of the inhibitor at 303 K, 313 K, 323 K, 333 K and 343 K. The results are presented in fig (1). IE decreased with increase in temperature at lower concentrations. With higher concentrations of inhibitor IE increased with increase in temperature up to 333 K. Further increase in temperature showed a decrease in efficiency. The decreased protection efficiency at high temperature might be explained from the fact that increase of temperature affected the rate of adsorption / desorption ratio and if the rate of desorption was faster than the rate of adsorption, there might be decrease in inhibition efficiency with temperature ^[12].

Figure - 1



Adsorption Isotherm

It is generally accepted that the organic molecules inhibit corrosion by adsorption at the metal/solution interface and that the degree of adsorption depends on the molecules chemical structure, chemical composition of the solution, the nature of metal surface, the temperature and the electrochemical potential at the metal/solution interface. ^[13]

The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metal has been deduced in terms of adsorption characteristics of the inhibitor. The surface coverage (θ) values are very useful while discussing the adsorption

characteristics. The surface coverage of the inhibitor at a given concentration is calculated by using equation,

$$\theta = (1 - r/r_0) \quad \dots\dots\dots (1)$$

Where r and r_0 are the corrosion rate with and without inhibitor respectively.

Langmuir Isotherm was tested for its fit to the experimental data.

$$\text{Log} [\theta / 1 - \theta] = \text{log } K + \text{log } C \quad \dots\dots\dots (2)$$

A plot of $\text{log} (\theta/1-\theta)$ Vs $\text{log } c$ was a straight line Figure (2) indicating that the MF under investigation obey Langmuir adsorption isotherm. Straight line obtained by plotting θ Vs $\text{log } c$, Figure (3) revealed that the adsorption of MF could be fitted with Temkin isotherm also. The experimental data are fitted with both Langmuir and Temkin adsorption isotherms. This indicates that the main process of inhibition is by adsorption.

Figure - 2

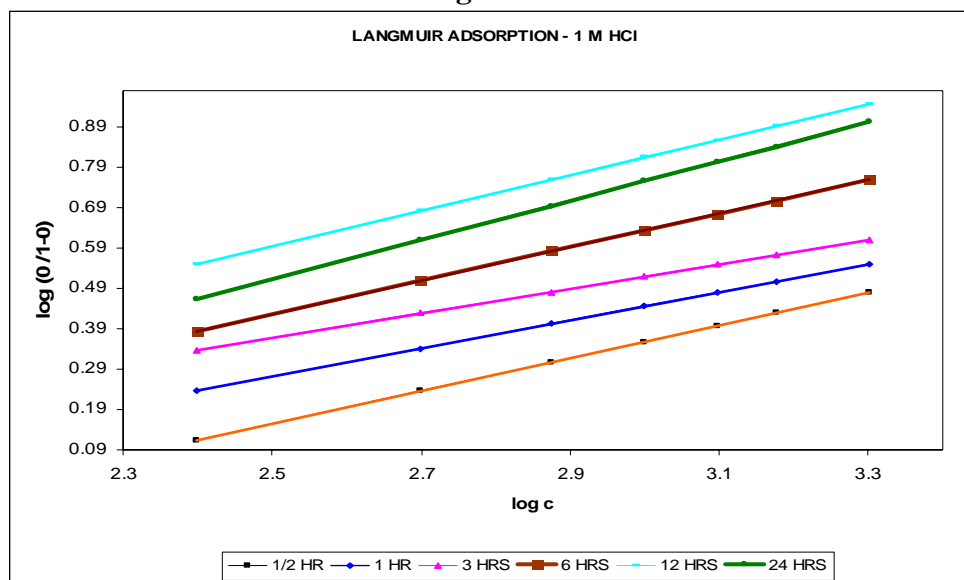
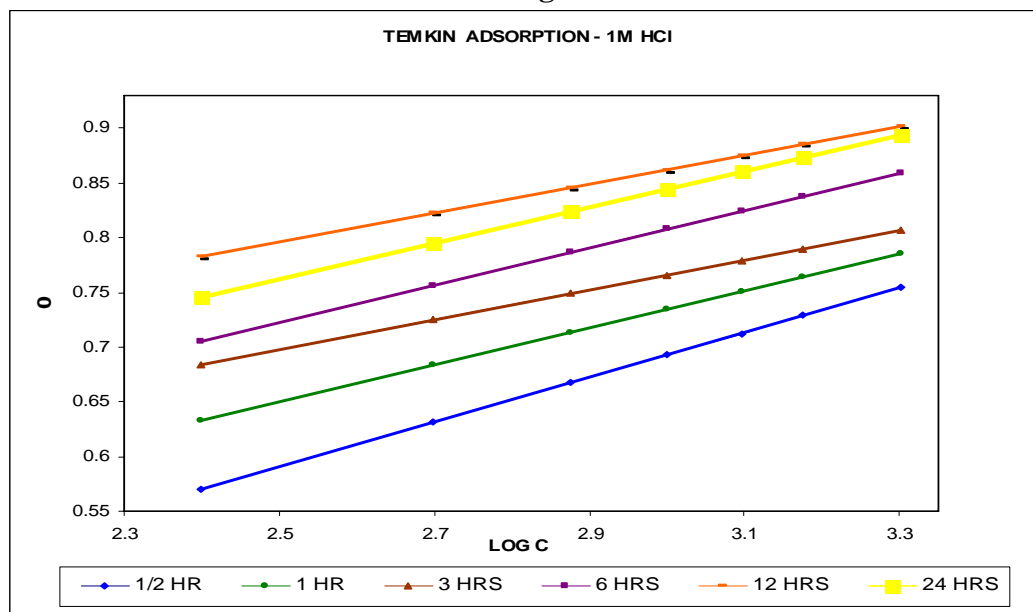


Figure - 3



Energy of Activation E_a and Thermodynamic parameters

The dependence of logarithm of the corrosion rate on the reciprocal values of the absolute temperature gives straight line. The values of the slope of these straight lines permit the calculation of activation energy E_a by the application of equation,

$$C. R = A. e^{(-E_a / RT)} \dots\dots\dots (3)$$

where A is the frequency factor for the reaction, R is the universal gas constant, T is the temperature (Kelvin). Thus E_a can be evaluated from the rate constant at any temperature. The decrease of E_a value (Table-2) in the presence of inhibitor proves the chemisorption of the inhibitor^[14]. Change in free energy values of adsorption (ΔG_{ads}) at different temperatures were calculated from Gibbs Helmholtz equation.

$$\Delta G = \Delta H - T \Delta S \dots\dots\dots (4)$$

Where ΔS is entropy of adsorption and ΔH is enthalpy of adsorption. The negative free energy values (Table -2) indicate spontaneous adsorption and a strong

interaction between the inhibitor molecules and the metal surface. The positive values of ΔS also supports the strong interaction between the inhibitor molecules and mild steel. These observations coupled with increase in inhibition efficiency with temperature and decrease in free energy of adsorption with temperature are suggestive of chemisorptions of the inhibitor on the surface of mild steel ^[15].

Table -2

Kinetic and Thermodynamic Parameters of MS in the presence of MF extract

Concentration of the inhibitor in ppm	Activation Energy E_a KJ/mole	Free Energy of Adsorption - $\Delta G =$ KJ/mole					Change in enthalpy ΔH J/mole	Change in Entropy ΔS J/mole
		303 K	313 K	323 K	333 K	343 K		
250	17.72	14.82	14.72	14.61	14.51	14.41	-17930	10.26
500	18.43	13.50	13.43	13.37	13.31	13.25	-4590	601.04
750	20.15	13.14	13.06	12.98	12.91	12.83	-3500	1232.832
1000	22.02	12.55	12.50	12.44	12.39	12.34	-3320	701.967
1250	18.65	12.15	12.09	12.04	11.98	11.93	-870	1037.545
1500	19.30	12.05	11.99	11.94	11.88	11.82	-420	1026.60
2000	17.99	11.63	11.59	11.54	11.50	11.46	-2620	747.569

Electro chemical Measurements

Potentiodynamic polarization studies

To find out the nature of the inhibitor, mode of action, mechanism of reaction, electrochemical measurements were carried out. The electrochemical data E_{corr} , I_{corr} Tafel constants b_a and b_c , for mild steel in acid corrosion in the presence and absence of the inhibitor are given in table.(3) In HCl solution without the inhibitor the value of R_p was low (11.23) and that of I_{corr} was high (2.87 mA/cm²) which confirmed that MS suffered maximum corrosion. The remarkable inhibition by MF was shown by the decrease in I_{corr} values and was confirmed by an appreciable increase in the R_p values which are given in table (4)

Table - 3

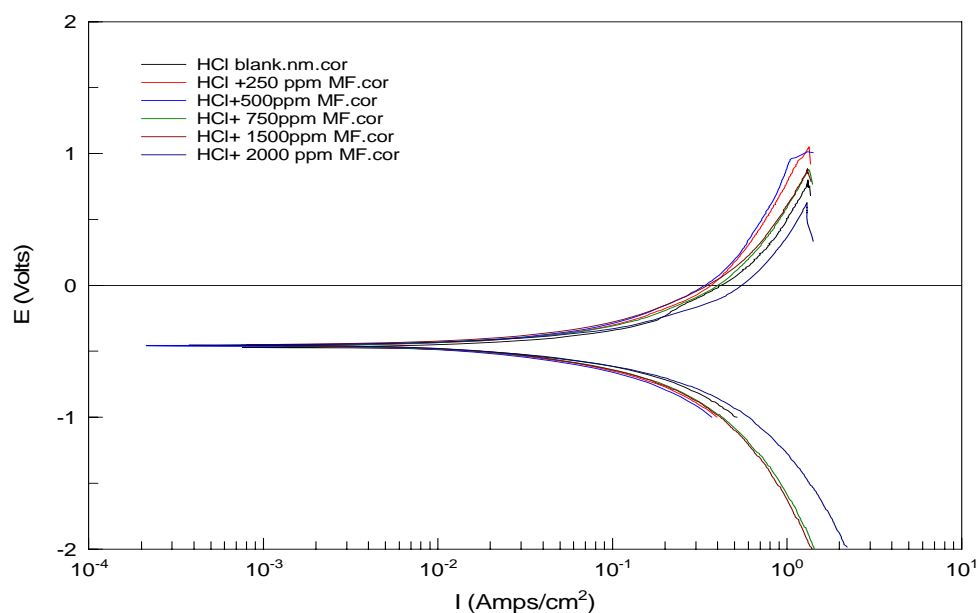
Polarization data of MS in the presence of MF

Concentration of the inhibitor in ppm	E_{corr} Mv / sec	I_{corr} mA/cm ² 10^{-2}	b_a mV / dec	b_c mV / dec	IE %
Control	-467	2.87	99	85	
250	-459	1.05	174	137	63.41
500	-458	0.922	207	165	67.87
750	-457	1.07	205	157	62.72
1500	-450	0.948	133	111	66.97
2000	-452	0.921	83	71	67.91

There is no noticeable change in the values of E_{corr} in the absence and presence of the inhibitor. This indicates the mixed nature of the inhibitor. Tafel constants b_a and b_c are found to be changing with the concentration of the inhibitor. This infers that the inhibitor reduces H_2 evolution as well as metal dissolution process. IE was found to 67.91% using I_{corr} values at 2000 ppm concentration.

Figure - 4

Polarisation curve of MS in presence of Myristica Frangans extract in 1M HCl



Electrochemical Impedance studies

The corrosion behaviour of mildsteel in acid solution in the presence of MF in 1M HCl was investigated by EIS at room temperature .Various impedance parameters such as charge transfer resistance (R_{Ct}), Double layer capacitance (Cdl) and the corresponding IE calculated are given in the table (4).

Table- 4

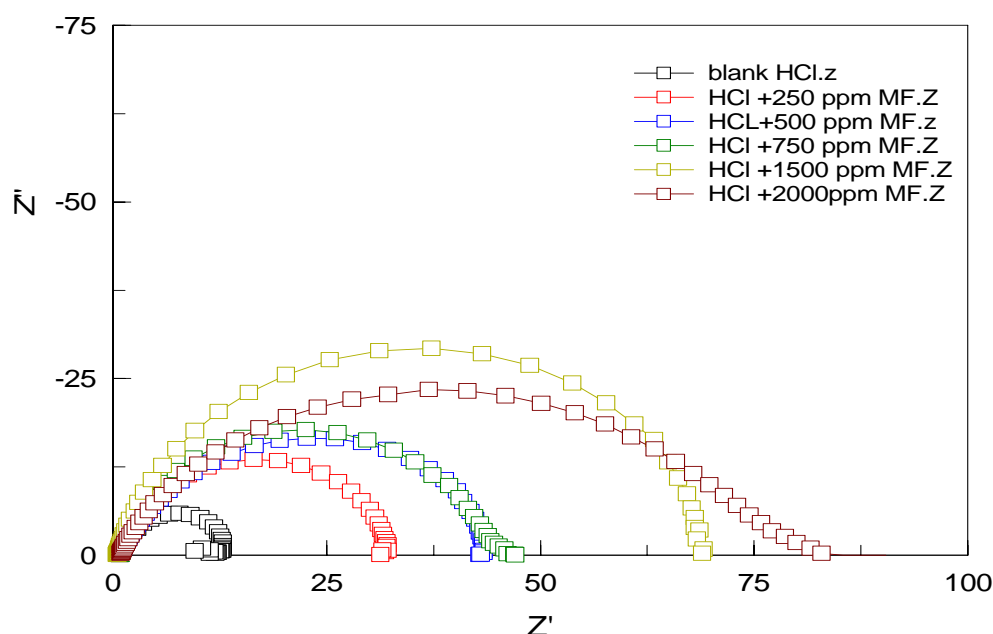
Electrochemical data for the corrosion of Mild Steel in 1M HCl

Conc of the inhibitor in ppm	R_{Ct} Ohm / cm ²	IE %	Cdl $\mu F / cm^2$	θ	R_p Ohm / cm ²	IE %
Control	12.22		46.64		11.23	
250	43.90	72.21	44.93	0.32	43.20	74.00
500	42.78	71.44	45.18	0.31	45.20	75.15
750	56.86	78.51	35.90	0.45	45.79	75.47
1500	68.95	82.31	33.28	0.49	45.07	75.08
2000	81.10	84.93	15.61	0.76	46.08	75.62

From the impedance parameters, it can be seen that as the MF concentration increases R_{Ct} values were found to increase but Cdl values tend to decrease. The decrease in Cdl values indicates the adsorption of MF molecule on the metal surface. Decrease in Cdl can result from a decrease in local dielectric constant or an increase in thickness of the electrical double layer, suggests that the MF function by adsorption at the metal solution interface.^[16] The change in R_{Ct} and Cdl values are caused by the gradual replacement of water molecules by adsorption of the organic molecules on the metal surface decreasing the extent of dissolution reaction.^[17] The semi circle obtained for the present system indicates that the adsorption of inhibitors molecule are charge transfer controlled. The increase of R_p with concentration of MF understudy indicate the effective inhibitive action of the inhibitor. Maximum IE using R_{Ct} values is found to be at 81% and 75.62 % using R_p values at 2000 ppm concentration. The surface coverage was found to be 0.76 using Cdl values.

Figure - 5

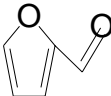
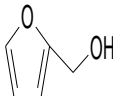
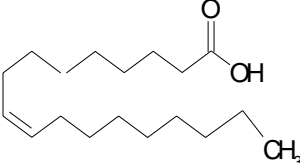
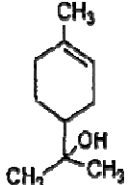
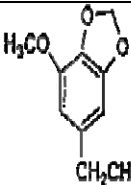
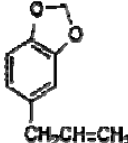
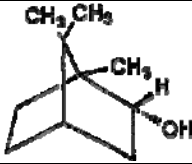
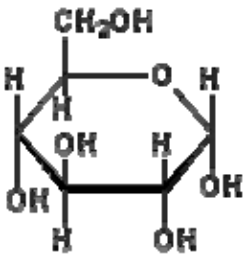
Nyquist Plots of Mild Steel in 1M HCl with MF

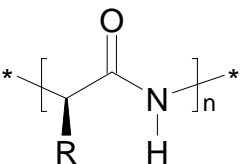


Probable Mechanism of Inhibition

From the wt loss measurements and chemical measurements, it was clear that the MF extract in acid medium behaves as a mixed type indicator by reducing H_2 evolution and metal dissolution process. This extract has been adsorbed on the mild steel surface which was understood from Langmuir & Temkin adsorption isotherms. Activation energy values and thermodynamic parameters also confirm that there is strong interaction between the extract & MS surface. The mechanism of inhibition of corrosion is generally believed to be due to the formation and maintenance of a protective film on the metal surface. The polar units (i.e.) hetero atoms like oxygen present in the inhibitor is acting as reaction centre for adsorption process. The phyto chemical constituents present in the extract is enlisted. ^[19] in the table (5).

Table - 5

S.No	Constituent	Structure	Concentration in ppm
1	Furfural		15,000
2	Furfurol	 =	15,000
3	Oleic acid		13,000 - 1, 76, 000
4	Alpha terpineol		120 - 9,600
5	Myristicin		800 - 12,800
6	Safrole		120 - 2,720
7	D-bureneol		4,200 - 25,600
8	Carbohydrate	 alpha-D-Glucopyranose	285,000

9	Protein		58,000 - 75,000
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The constituents of the extract mostly composed of Oxygen and Nitrogen containing compounds. Adsorption of constituent may occur either through N or O active centre. The constituents also contain OH groups around the molecules. This makes them more ready to form strong links with metal surface. In addition they may form complexes with metal cations, which are sparingly soluble in aqueous environment. The complexes have been suggested.^[18] to cause blocking of micro anodes and/or micro cathodes that are generated on the metal surfaces when in contact with electrolytes, and so can retard the subsequent dissolution of the metal.

CONCLUSION

- Acid extract MF is found to be an effective inhibitor for mild steel in acidic medium giving up to 90.91% efficiency
- Inhibition efficiency increases with inhibitor concentration.
- The inhibitor used in the current study followed Langmuir and Temkin adsorption isotherm.
- Polarization curves obtained in the presence of the MF extract indicates that it behaved as a mixed type inhibitor
- Biodegradable Green Inhibitor Myristica Frangans can be safely used without hydrogen damage toxic effects and pollution problems

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