## Summary

1. The aim of the present work was to prepare organic corrosion inhibitors for overhead distillation towers of petroleum processing, from some local cheap raw materials, and to evaluate them under conditions which are not far removed from those prevailing in pratice. Various mechanisms have been suggested to correlate the molecular structure of organic inhibitors with their inhibiting efficiency. The problem is still far from being clearly established.

   The main theme of the present work was thus, the correlation between the structure of the prepared inhibitors and their efficiency. Percentage inhibition as high as 92% could be achieved both in the liquid and gas phases. A mechanism has been suggested based on, the availability of the unshared pair of electrons on the nitrogen atoms in the molecule, as well as the branching of the molecule.

2. The literature survey covered the types of inhibitors used for corrosion inhibition in refineries, methods of preparations, theories of inhibition mechanisms, and factors affecting inhibitors efficiency.

3. The experimental part includes all the details about apparatus, methods of preparations, analysis and evalua-

tion of inhibitors, both in liquid and gas phases.

In the present work, fourteen inhibitors were prepared by the reaction of epoxidized linseed oil and epoxidized oleic acid with aliphatic and aromatic amines. They are:

a. Epoxidized linseed oil modified with methyl, ethyl and butyl amines; aniline, p-chloroaniline, p-toluedine p-anizidine.

b. Epoxidized oleic acid modified with the same aliphatic and aromatic amines, mentioned in "a".

Inhibitor efficiency was measured in the liquid phase by immersing carbon steel coupons in 0.05 N HCl solution containing the inhibitor, at 70°C for 1½ hr. In the gas phase experiments, hot steel coupons were sprayed with inhibitor solution, and then exposed to a mixture of gasoline and 2 N HCl vapours. The percent inhibition values were calculated from weight loss measurements in the presence and absence of inhibitors. The inhibitor concentrations were 10 - 50 and 10 - 100 ppm in liquid and gas phases, respetively.

4. In the liquid phase, inhibition of aliphatic amines increased in the order, methyl $<$ ethyl $<$ butyl for

modified epoxidized linseed oil (M.E.L.O.), and butyl < ethyl < methyl for modified epoxidized oleic acid (M.E.O.A.). At 50 ppm, P.I. values of methyl-, ethyl- and butylamines amount to 39.75, 42.16, and 43.90 for M.E.L.O., and 92.16, 91.66 and 90.43 for M.E.O.A., respectively.

In the gas phase , the order of inhibition for both M.E.L.O. and M.E.O.A. is methyl < ethyl < butyl. At 100 ppm the P.I. values of methyl-, ethyl- and butylamines amount to 80.09, 88.50 and 92.43 for M.E.L.O. and 75.20, 81.89 and 87.11 for M.E.O.A., respectively.

5. Inhibition of aromatic amines increased in the order p-chloroaniline < aniline < p-toluidine < p-anizidine, for M.E.L.O. and M.E.O.A., both in liquid and gas phases. In the liquid phase, the P.I. values amount to 25.82, 39.58, 52.21 and 59.43 for M.E.L.O., and 88.01, 91.83, 93.31 and 94.57 , for M.E.O.A., respectively. The P.I. values in the gas phase amount to 70.32, 77.52, 84.22 and 85.93, for M.E.L.O. and 62.53, 67.87, 71.50 and 74.03, for M.E.O.A., respectively.
6. The increse of inhibitive efficiency of aliphatic amines, in the gas phase passing from methyl- to butyl-amine, is in the line with the prediction based on Taft constant. According to this prediction, the reactivity of the functional group (>NH) with the atoms of the metal surface,

for co-ordinate bond formation, increases with increase in the length of the alkyl chain.

7. The results obtained for aromatic derivatives of E.L.O. and E.O.A., both in liquid and gas phases, reveal a linear relationship between P.I. and both Hammett constants and basicity.
8. Nuclear magnetic resonance (N.M.R.) was made for E.L.O. and aromatic amines, individually and during their reactions. The epoxy group bands were shifted up-field and their values were dependent on basicity and Hammett constant of the amine. It was found that, p-toluidine causes higher epoxy shift and possesses higher P.I. values than aniline and p-chloroaniline.
9. The results for M.E.L.O. and M.E.O.A. with aliphatic and aromatic amines, conform with Langmuir adsorption isotherms. For M.E.O.A., the slopes of the straight lines were nearly of unit gradient. For M.E.L.O., the slopes deviated from unity.
10. The results were interpreted in the light of a model which assumes that, both the size of the molecule and the electron density on the nitrogen atom control the efficiency of the inhibitor.

In the liquid phase, M.E.L.O. molecule is anchored to the metal surface through two nitrogen atoms, whereas the third projects away from the surface. The projecting arms of the molecules, having polar ends, repel each other leading to relatively low P.I. values. M.E.O.A. being less branched than M.E.L.O. does not suffer from a projecting polar arms. This structure difference leads to, relatively, higher P.I. values for M.E.O.A. .

In the gas phase, adsorbed water dipoles are not encountered, and the conditions are favourable for the anchoring of the M.E.L.O. molecule through the three nitrogen atoms. This results in a marked increase in the P.I. values (much higher than that in the liquid phase). M.E.O.A. is less efficient than M.E.L.O. because the latter possesses larger molecular size, and is anchored to the metal surface through three nitrogen atoms, in stead of two for the former. Branching is favourable for both M.E.L.O. and M.E.O.A., as judged from the increase of P.I. with increasing the length of the alkyl chain.

11. The linear relationship between P.I., Hammett constants, basicity and epoxy group shift of the prepared compounds, furnishes support for the interpretation of inhibition in terms of electron withdrawing and electron repelling substituents in the aromatic ring.

12. In the liquid phase, aromatic amines in M.E.L.O. are less efficient than the corresponding derivatives of M.E.O.A. . The opposite behaviour is encountered in the gas phase. This behaviour accords with that obtained for aliphatic amine derivatives and was interpreted along the same lines.

13. Two commercial inhibitors, namely Kontol-CL 23 and Sepacorr-SC , were tested and the results were compared with those of the prepared ones. In the liquid phase, the order was, p-chloroaniline in M.E.L.O. < Sepacorr SC < methyl-, ethyl- and butyl-amines and aniline, p-toluidine and p-anizidine in M.E.L.O. < p-chloroaniline in M.E.O.A. < Kontol-CL 23 < methyl- and ethyl-amines and aniline, p-toluidine and p-anizidine in M.E.O.A. . In the gas phase, the order was Sepacorr-SC < p-chloroaniline in M.E.O.A. < Kontol-CL 23 < all aliphatic and aromatic amines both in M.E.L.O. and M.E.O.A. .