5. RESULTS AND DISCUSSION

5.1. Results and Discussion of Inhibitor Preparation

5.1.1. Thermal stability of epoxidized linseed oil:

The thermal stability of epoxidized linseed oil at 130°C in the absence of any reagents was tested before studying its reaction with amines. The epoxidized linseed oil was heated at that temperature for different periods of time. The oxirane content was then determined by volumetric titration against 0.1N HBr in acetic acid. The results are collected in Table 1, where V_0 and V are the volumes of HBr consumed before and after heating for different times, respectively. It is clear that, after 3, 6, 10 and 24 hours, the amount of the degraded epoxidized oil are 0.22 %, 0.41 %, 0.5 % and 0.7 %, respectively. These values indicate high thermal stability of the epoxy group in epoxidized linseed oil, when no other reagents are present.

5.1.2. Reactions of aromatic amines with epoxidized linseed oil:

In the present work aromatic amines (aniline, p-chloroaniline, p-toluidine and p-anisidine) were taken as a model

Table (1): The effect of heat on epoxidized linseed oil at 130°C for different periods of time.

Time (hrs)	mls of HBr*	Oxirane content (%)	$\frac{V}{V_o}$ x 100
0	34.37	5.50	100.0
$\frac{1}{4}$	34.30	5.49	99.7
$\frac{1}{2}$	34.17	5.47	99.4
$\frac{3}{4}$	33.91	5.43	98.7
1	33.75	5.41	98.2
2	33.44	5.35	97.3
3	33.00	5.28	96.0
4	32.63	5.22	94.9
5	32.19	5.15	93.7
6	31.81	5.09	92.6
10	31.25	5.00	90.9
24	30.00	4.80	87.3

*. ml of 0.1N HBr required for one gram sample.

Table (2): The effect of time on the reaction of aniline, p-toluidine, p-anisidine, and p-chloroaniline with epoxidized linseed oil.

Time (hrs.)	Aniline		p-Toluidine		p-Anisidine		p-Chloro-aniline	
	HBr*	$\frac{V}{V_o}$x100	HBr	$\frac{V}{V_o}$x100	HBr	$\frac{V}{V_o}$x100	HBr	$\frac{V}{V_o}$x100
0	55.70	100.0	59.25	100.0	27.14	100.0	51.20	100!0
1/4	53.61	95.6	55.84	94.24	26.93	99.2	48.90	96.75
1/2	50.45	90.57	51.37	86.70	26.43	97.40	48.10	93.90
3/4	48.20	86.54	49.01	82.71	25.86	95.30	47.26	92.30
1	46.11	82.78	47.18	79.63	25.28	93.10	46.11	90.005
2	45.35	81.42	45.25	76.37	24.15	89.00	44.61	87.12
3ù	45.00	80.79	44.58	75.24	24.00	88.40	43.72	85.40
4	44.58	79.84	43.65	73.67	23.91	88.10	43.09	84.16
5	44.40	78.71	43.35	73.16	23.85	87.90	42.63	83.26
6	---	---	43.14	72.80	---	---	42.50	83.00
10	---	---	---	---	---	---	42.30	82.60
24	---	---	40.77	68.80	22.80	84.00	41.42	80.90

*. mls of HBr required for one gram sample.

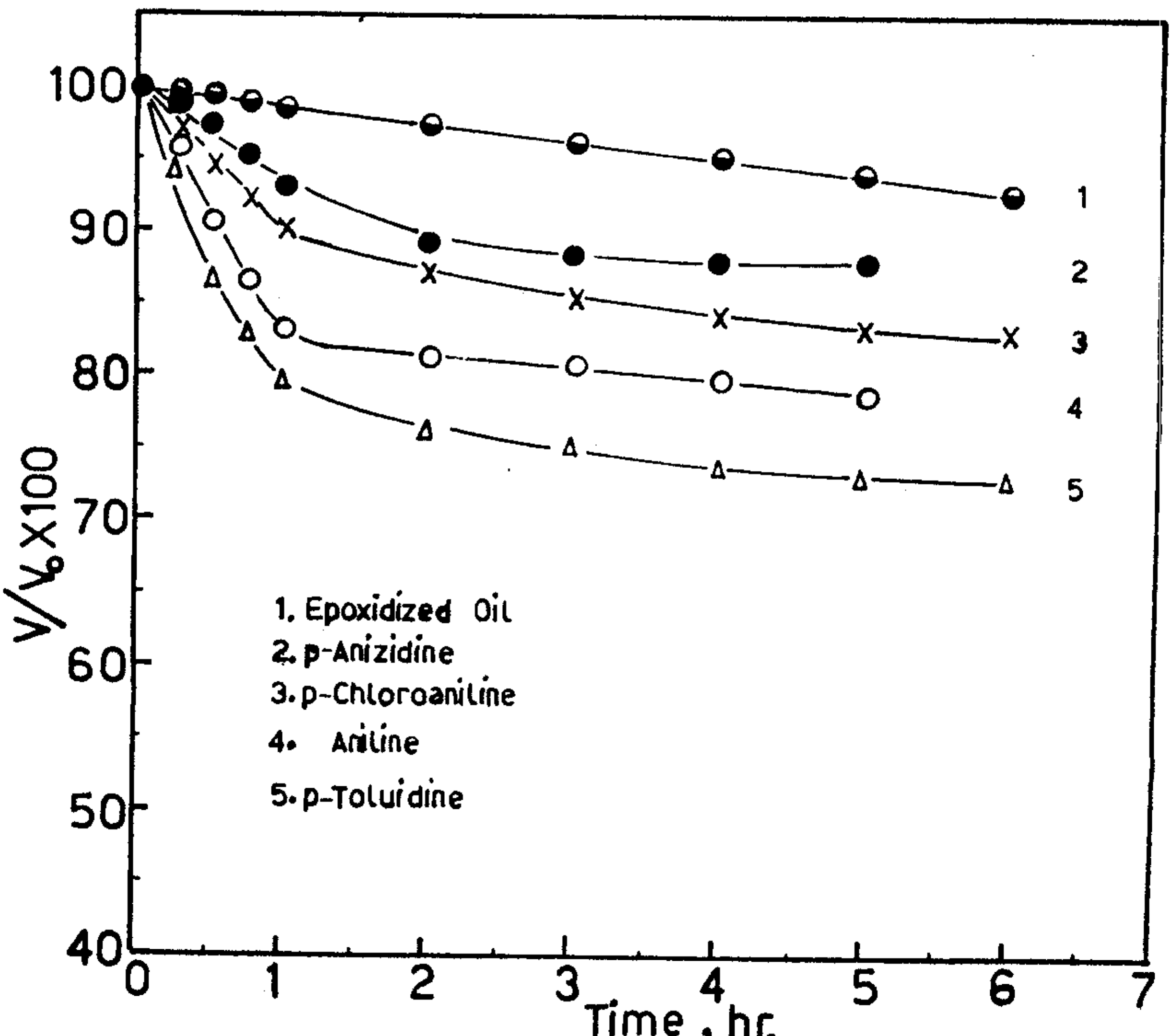


Fig. 4. Relationship between time and the rate of epoxy group fission at 130°C in the presence and absence of amines.

5.1.3. Effect of basicity and Hammett constants of amines on the rate of their reactions with epoxy compounds:

The values of basicity (pK_a) and Hammett constants (σ) for aniline, p-chloroaniline, p-toluidine and p-anisidine are given in Tables 3 and 4, respectively. Figures 5 and 6 show plots for the rate of epoxy group fission against basicity and Hammett constants, respectively. The rate is calculated from the volume of HBr consumed before carrying out the reaction (V_o), and the volume consumed after different times (V). These relations are found to be straight lines for all reaction times. It can be, also, seen that as the reaction time increases, these lines approach each other until they coinside, indicating, approximately, a complete consumption of the epoxy groups present.

It is clear from Fig. 5 that, the basicity of the amine plays a significant role in the degree and extent of epoxy group fission, where the reaction rate is seen to increase with increasing basicity. The results obtained in Fig. 6 shows also that, the Hammett constant is a measure of the reaction rate of epoxy group with amines. Negative values of Hammett constant which quantitatively indicate high electron density on the nitrogen atom, imply higher rate and extent of fission of the epoxy group.

Table (3): The values of basicity (pK_a) of aromatic amines

R	Index	Basicity (pK_a)
H	$NH_2-C_6H_5$	4.63
CH_3	$NH_2-C_6H_4-CH_3$	5.08
OCH_3	$NH_2-C_6H_4-OCH_3$	5.34
Cl	$NH_2-C_6H_4-Cl$	4.15

Table (4): The values of Hammett constants (σ) of aromatic amines

R	Index	Hammet constant
H	$NH_2-C_6H_5$	0.000
CH_3	$NH_2-C_6H_4-CH_3$	- 0.170
OCH_3	$NH_2-C_6H_4-OCH_3$	- 0.268
Cl	$NH_2-C_6H_4-Cl$	+ 0.227

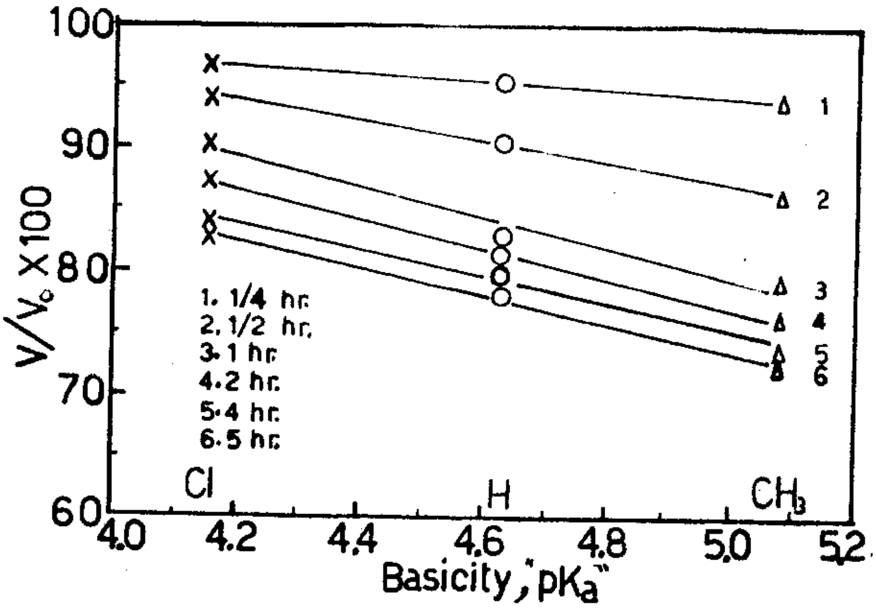


Fig. 5. Relationship between basicity of amines and the rate of epoxy group fission at different times.

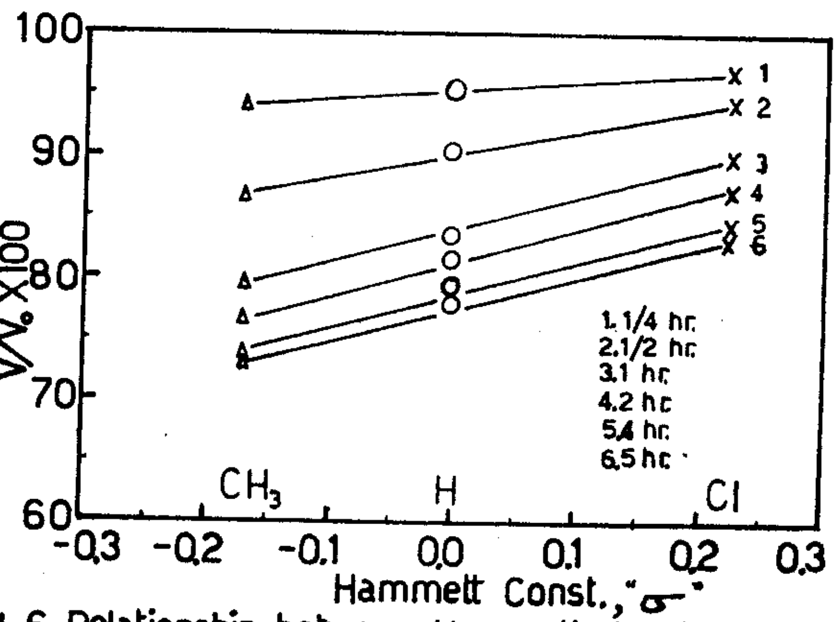


Fig. 6. Relationship between Hammett Constants of amines and the rate of epoxy group fission at different times.

5.1.4. Nuclear magnetic resonance of amines and epoxidized compounds:

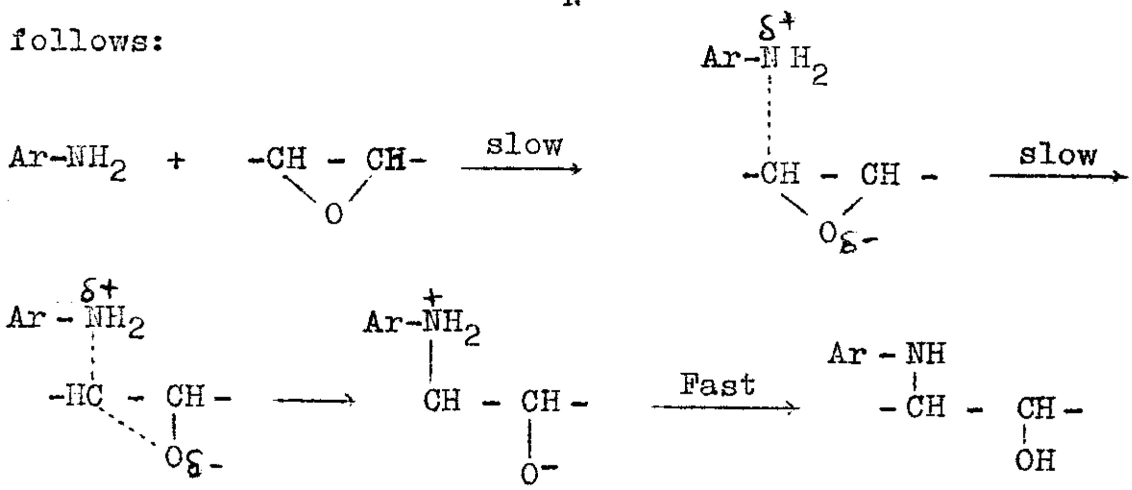
The reactions of aromatic amines with epoxidized linseed oil were also followed by nuclear magnetic resonance (N.M.R.). It was found that both epoxy and amino group bands were shifted as soon as the stoichiometric amounts of amine were added to epoxidized oil. The amino group bands are moved down-field, whereas the epoxy group bands are moved up-field, for amine-epoxidized linseed oil mixtures, as shown in Table 5.

Figures 7 and 8 show plots of basicity and Hammett constants against N.M.R. epoxy group shifts, respectively. These relations are found to be straight lines. It is clear from Fig. 7 that, the values of N.M.R. epoxy group shifts, which indicate the rate of reaction, increase with increasing basicity. Figure 8, on the other hand, shows that, the epoxy group shifts increase with increase of electron density on the nitrogen atom of the amine as indicated by the negative values of Hammett constant. These relations support the contention that, the reaction rate of amines with epoxidized compounds depends both on basicity and Hammett constants.

Table (5): N.M.R. group band shifts (in Hz) upon addition of aromatic amines to the epoxidized linseed oil.

R	Index	NMR group band shifts (Hz)	
		Amino group	Epoxy group
H	$E_p-NH_2-C_6H_5$	-7	5.5
CH_3	$E_p-NH_2-C_6H_4-CH_3$	-7	7.5
OCH_3	$E_p-NH_2-C_6H_4-OCH_3$	-12	4.0
Cl	$E_p-NH_2-C_6H_4-Cl$	-7	3.0

From these studies, it can be concluded that, the reaction mechanism of epoxy group in epoxidized fatty materials with aromatic amines is of S_N2 type and may be expressed as follows:



The experimental results discussed above are in accord with this proposed mechanism.

Conclusions:

From the above results, it can be concluded that :

1. The epoxy group in the epoxidized oils are stable for long periods at temperatures up to 130°C.

2. The rate and extent of fission of epoxy groups in their reaction with amines, is dependent on basicity and Hammett constants.

3. The reaction of epoxy groups with aromatic amines proceeds according to S_N2 mechanism.