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SEPARATION OF NITROGENOUS TYPE COMPOUNDS
FROM SYNTHETIC CRUDES

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ABSTRACT

An adsorbent has been tested to selectively remove nitrogenous compounds from synthetic crudes. The adsorbent is an ilmenite ore treated with liquid bromide. The bromination step forms titanium and iron bromides on the surface; these species are Lewis acids and are known to form complexes with nitrogenous compounds.

Separation using this adsorbent is only partially successful. The results show that basic nitrogenous compounds are extensively retained on treated ilmenite while neutral compounds are not. Thus, the adsorption capacity is high for basic compounds but low for neutral compounds.

A coker kerosene was used to test the adsorbent. Nitrogenous compounds were found in the effluent after only a few millilitres were fed into the column.

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LA SEPARATION DES COMPOSES AZOTES TYPIQUES DES HUILES SYNTHETIQUES

par

G.Jean*, M.Poirier* and H.Sawatzky**

RESUME

Nous avons mis au point un adsorbant pour enlever sélectivement les composés azotés contenus dans les pétroles synthétiques. L'adsorbant est de l'ilménite, préalablement traité avec du brome. Le brome réagit avec l'ilménite formant des bromures de titane et de fer; ces composés sont des acides Lewis et forment des complexes avec les composés azotés.

Le succès de cette méthode de séparation, n'est que partiel. Les résultats montrent que les composés azotés basiques sont retenus par l'ilménite et que les composés azotés neutres le sont beaucoup moins. Donc, la capacité d'adsorption est grande pour les composés basiques et faible pour les composés neutres.

Nous avons utilisé un kérosène pour tester cet adsorbant. Les composés azotés apparaissent dans l'effluent après seulement quelques millilitres.

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INTRODUCTION

Nitrogenous compounds in crude oils and petroleum products have been associated with several problems in recovery and processing operations. They contribute to the emulsion problem encountered in the hot water separation process of bitumen from tar sand, to catalyst deactivation during upgrading, and to gum formation in oils and fuels during storage (1,2).

For these reasons, nitrogen must be removed from the feedstock in the early stages of upgrading. This is done by severe hydrotreating at high pressures and temperatures which has several disadvantages: high capital cost investment, degradation of valuable material, and high operating cost due to hydrogen consumption.

A method allowing the separation of nitrogenous compounds from the feedstock would greatly reduce the cost of upgrading synthetic crudes, decrease capital cost requirements, improve process efficency by avoiding degradation and excessive hydrogen/energy requirements, and permit optimum use of the nitrogenous compounds.

Several analytical procedures are known for the separation and characterization of nitrogenous compounds. Jewell and Snyder used complex formation on supported ferric chloride and ion-exchange resins to isolate the "non-basic" nitrogenous compounds from petroleum(3). Ford et al. (4) employed alumina adsorption chromatography to separate the nitrogenous compound types while Guerin et al. (5) used acid-base extraction and Sephadex LH-20 column chromatography. Ben, Kovskii and Olzseova removed nitrogen compounds from diesel fuel by complexation with titanium tetrachloride(6). These methods are complex and are not designed for industrial scale. More recently Audech (7) developed a method for large-scale (gallons) removal of nitrogenous compounds from lubricating oils using anhydrous hydrochloric acid adsorbed on an alumina-silica catalyst(7).

Work at ERL has shown that various waste minerals could be used as low cost adsorbents for the removal of nitrogenous compounds from synthetic crudes. This paper describes the treatment of ilmenite and its adsorptive properties.

EXPERIMENTAL

Treatment of Ilmenite

Ilmenite ore was crushed to about 74μm. The ore was taken from a site about 2.4 km southwest of St-Urbain and about 11.2 km north of the village of Baie St-Paul, Québec, on the north shore of the St.Lawrence River. Its elemental composition is given in Table 1. In a 100-mL round bottom flask equipped with a reflux condenser containing 15-g crushed ilmenite an excess of bromine (about 10 mL) was added. The mixture was heated at 58°C for 2 h,cooled, and the excess bromine washed with 50-mL pentane. The treated ilmenite was filtered and then washed again with pentane until the solvent became colourless. The treated ilmenite was then dried with a stream of nitrogen, and used as adsorbent. The treatment was also conducted at room temperature for 70 h.

REMOVAL OF NITROGENOUS COMPONENTS

A coker kerosene was obtained from Great Canadian Oil Sands. It's properties are given in Table 2. About 120 mL sample of coker kerosene was percolated through a column packed with 10-g brominated ore. Eight fractions of the eluate were collected (two 5-mL and six 10-mL fractions) and analyzed·for total nitrogen using a Dohrmann micro-coulometer Model C-200B.

MODEL COMPOUND STUDY

To understand the adsorption mechanism, a standard solution of 18 nitrogenous compounds in toluene was prepared. Its composition is given in Table 3.

This solution was pumped continuously at 0.5 mL/min. into a 30 cm long x 0.4 cm I.D. column, packed with 20 g treated ilmenite. A fraction collector was used to collect 5-mL samples which were subsequently analyzed using a Varian 6000 gas chromatograph equipped with a 12.5 m long SE-30 capillary column.

CALCULATION

The percentage of each compound in each sample of effluent was calculated by comparing the corresponding peak area of the gas chromatogram for a particular sample with the area of this peak for the original solution.

$$\% \text{ Species } i = \frac{\text{area of peak } i \text{ in sample}}{\text{area of peak } i \text{ in feed}} \times 100$$

$$\% \text{ Total nitrogen} = \frac{\sum \text{ Area of peak } i \text{ in sample}}{\sum \text{ Area of peak } i \text{ in feed}} \times 100$$

No error analysis was done on these results.

RESULTS AND DISCUSSION

Industrial separation methods are significantly different from those of analytical separation. Analytical separation methods use only a very small portion of the available sites of the adsorbent; under these conditions the distribution isotherm is linear and there is no competition between compounds. In large scale separation methods the feed is pumped continuously to the adsorbent bed until saturation of all sites occurs. At this point adsorption is no longer possible and breakthrough occurs, i.e., the concentration of the solute in the effluent increases to its original concentration. The breakthrough point is a measure of the capacity of the adsorbent.

The breakthrough curve was measured for the standard feed containing 18 nitrogenous compounds. Figure 1 gives the percent nitrogenous compounds in

the feed vs volume pumped into the column. Breakthrough (curve 2, Fig. 1) occurs around 40-60 mL: below that volume most of the nitrogenous compounds are retained by the brominated ilmenite.

An X-ray photoelectron spectroscopy (XPS) study of the brominated ilmenite showed the presence of $TiBr_x$ and $FeBr_x$ on the surface. These salts are readily soluble in methanol and methanol washed ilmenite lost its adsorption capacity for nitrogenous compounds (curve 1, Fig. 1). The methanol solution extracted most of the bromide salts as evidenced by the dark-brown colour of the extract. These results suggest that the bromide salts are responsible for the adsorption of the nitrogenous compounds.

To gain more insight into the mechanism of adsorption the effluent was analyzed by gas chromatography (GC). This analysis showed that the 18 compounds have significantly different adsorption properties. Figure 2 gives the individual breakthrough curves. These results show that some compounds such as benzyl-amine and 2,2[1] dipyridyl are extensively adsorbed by the treated ilmenite. These compounds are still completely retained by the ilmenite after 150 mL has been pumped into the column. Other compounds such as carbazole and indole are not extensively adsorbed and elution occurs after 40 mL. The amount of benzylamine adsorbed is at least 10 times that of carbazole. Table 4 gives the order of elution of the 18 compounds and the pK_a and proton affinity of the compound where possible. There seems to be a general correlation between the extent of adsorption and the basicity of the compound. Carbazole is acidic and elutes immediately while very basic compounds such as dibenzylamine and 2,2[1] dipyridyl etc. are still totally retained after 150 mL.

Another important feature observed in Fig. 2 is that some compounds are irreversibly adsorbed while others are reversibly adsorbed. Compounds such as 3-methylindole, indole and tetrahydrocarbazole are irreveribly adsorbed, in other words these compounds have saturated the sites that were available to them and were not subsequently desorbed. Conversely, compounds such as aniline, 2-phenyl-pyridine and 3,4-benzacridine are reversibly adsorbed. Their behaviour is typical of displacement chromatography where a compound is desorbed by another thus giving rise to a concentrated front that eventually elutes in the effluent. Figure 2 shows that these compounds elute in the effluent at a concentration of about three times that of the original feed. A rough mass balance indicates that these compounds are quantitatively desorbed and practically none is left on the column after the concentrated front has eluted. For this study, compounds were subdivided into four classes according to their adsorption behaviour (Table 5 and Fig. 4).

Class 1 is composed of carbazole, tetrahydrocarbazole, indole, 3-methylindole, and phenothiazine. These compounds are not extensively retained (first five breakthrough curves in Figure 2) and were irreversibly adsorbed. There is a striking similarity between these compounds; they are all acidic/neutral having a pyrrole ring (except phenothiazine) and a proton on the nitrogen atom. This similarity is used to explain their adsorption mechanism.

It is well known that titanium halides will react with primary and secondary amines to form a complex (8). Nitrogenous compounds with an active hydrogen can displace halides to give complexes $X_2Ti(NHR)_2$ or $X_3Ti(NR_2)$. Similar reactions are probably occurring at the surface of the treated ilmenite for titanium and iron salts.

$$MX_x + n(NH_2R) \rightarrow X_{x-n}M(NHR)_n + nHBr \qquad \text{Eq. 1}$$

or

$$MX_x + n(NHR_2) \rightarrow X_{x-n}M(NR_2)_n + nHBr. \qquad \text{Eq. 2}$$

where M = Ti or Fe

X = halide

n = 1 or 2 depending on the nature of the amine

R = alkyl group

In this case adsorption is really a surface complexation. For purposes of this paper the term adsorption is used.

Class 3 is composed of trimethylpyrrole, n-octylamine, n-decylamine, and 2-aminochrysene. Every compound in this class (except trimethylpyrrole) is a primary amine and a strong base. These compounds are more quantitatively adsorbed than those of classes 1 and 2. They probably react with the surface according to Eq. 1 and are likely to be in competition with those of class 1. Note that compounds in class 1 were irreversily adsorbed which indicates that the following reaction did not take place.

$$X_{x-n}M(NR_2)_n + nNH_2R \rightarrow X_{x-n}M(NHR)_n + nNHR_2 \qquad \text{Eq. 3}$$
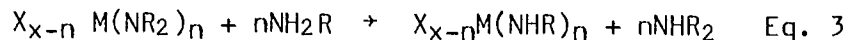
The more basic primary amines did not displace the compounds of class 1.

The difference in adsorption capacity between the various classes can be explained in terms of their relative basicity. The surface is made of sites of various activity. The site distribution is expected to ressemble a Boltzmann distribution where the highly active sites represent only a small fraction of

the sites. The extent of adsorption of the nitrogenous compounds with the surface Lewis acids will depend on the availability of the lone pair of electrons on the nitrogen atom. Compounds of class 1 are not basic and will react only with the highly active sites. These active sites represent only a small percentage of the total sites which explains the low level of adsorption of class 1 compounds. Compounds of class 3 and 4 are much more basic and will react with a much broader range of sites than those of class 1 and have a higher level of adsorption. Steric hindrance could also possibly play a role.

Contrary to class 1, class 2 compounds were reversibly adsorbed. These compounds are characterized by a weak basicity: all except aniline have a pyridine ring, are highly aromatic and do not have an active hydrogen on the nitrogen atom. One possible mechanism of adsorption is through the donation of the electron pair of the nitrogen to the Lewis centers. (Physical forces interactions of the pi electrons with the surface, and hydrogen bond formation are neglected). The reaction can be illustrated as follows:

$$X_xM \ + \ :NR_3 \ \rightarrow \ X_xM:NR_3 \qquad \qquad \text{Eq. 4}$$

Delocalization of the one pair of electrons over the ring decreases its availability for bonding and these compounds will form only weak bonds with the surface. This reaction is found to be reversible. The more basic compounds of class 3 and 4 probably displace compounds of class 2 according to the reaction:

$$X_xM:NR_3 \ + \ nNH_2R \ \rightarrow \ X_{x-n}M(NHR)_n \ + \ :NR_3 \ + \ nHBr \qquad \text{Eq. 5}$$

Class 4 compounds have the highest adsorption affinity for the surface. These compounds are basic and will react with a great portion of the sites. $2,2^1$ dipyridyl is particularly interesting. It does not have an active hydrogen but is known to be a strong ligand (9). It gives stronger complexes than ligands such as primary and secondary amines. It probably reacts with the surface in a way similar to that described by Eq. 4.

Finally, the treated ilmenite was tested for its ability to remove the nitrogenous compounds from a coker kerosene. As expected from the model

compound study, some nitrogenous compounds broke through immediately: after 10 mL. the nitrogen concentration in the effluent increased to 40 ppm. (Fig. 3). Treated ilmenite was much more effective in removing nitrogenous compounds than natural ilmenite. The nitrogenous compounds of the kerosene that are not being removed are probably the acidic/neutral types.

- CONCLUSIONS

The important parameters determining the economic feasibility and the success of a separation process using an adsorbent are: the effective adsorption capacity, the relative kinetics of the adsorption/desorption cycle, the durability of the adsorbent and the overall cost.

The effective capacity is that which can be used before the desorption cycle is started. This is defined in terms of the maximum tolerable nitrogen concentration in the effluent. The main problem with treated ilmenite is that the effective capacity is a function of the feed. Indeed this process is expected to be successful for feeds having basic nitrogenous compounds but not for those having acidic nitrogenous compounds and implies the capacity could vary greatly depending on the nature of the nitrogenous compounds in the feed, a result obviously not acceptable.

The durability of the adsorbent is also questionable. It was noted during our experiments that some of the complexes formed between the salts and the nitrogenous compounds were entrained in the effluent. Although in small concentrations, titanium and iron salts were found in the effluent. Durability is also affected by the presence of any trace of moisture which would hydrolize the metal-bromide bond and destroy the active sites while liberating toxic HBr.

In summary this study showed that some types of nitrogenous compounds could be selectively removed by using an adsorbent having a high concentration of Lewis acid sites and delineated the shortcomings of using treated ilminite as an adsorbent. They are:

- low effective adsorption capacity
- variation of the effective adsorption capacity with feed composition
- possible deterioration of the adsorbent due to hydrolysis
- low removal of certain nitrogenous compounds.

Therefore, treated ilmenite is not a feasible adsorbent for industrial use. However, this study suggests a new approach to design an effective adsorbent. The ideal adsorbent could separate these compounds by a non-acid/base interaction which would allow both acid and basic nitrogenous compounds to be separated indiscriminantly. A combination of acid/base interactions and other interactions could also give good results. Such an adsorbent has been identified and the results will be published soon.

References

1. A.A. Oswall and F.J. Noel, J. Chem. Eng. Data, 6, 294 (1961).

2. R.K. Artzmark and J.B. Gilbert, Hydrocarbon Processing, 46, 143 (1967).

3. D.M. Jewel and R.E. Snyder, J. Chromatog., 38, 351 (1968).

4. C.D. Ford, S.A. Holmes, L.F. Thompson and D.R. Latham, Anal. Chem., 53, 831 (1981).

5. M.R. Guerin, C-h Ho, T.K. Rao, B.R. Clark, J.L. Epler, Environ. Res. 23, 42 (1980).

6. V.G. Ben'Kovski and M.D. Olzseva, Chem. Techn. of Fuel and Oil, 474 (1979).

7. C.A. Audech, Preprint: Div. Petroleum Chem.: ACS meeting, Kansas City, Vol. 27, 998 (1982).

8. F.A. Cotton and G. Wilkinson; Advanced Inorganic Chemistry; Interscience Publishers; New York (1972): p.813.

9. C.K. Jorgensen, Oxidation Numbers and Oxidation States, Springer, New York, 1969, pp84-85.

10. G. Jean and H. Sawatzky, to be published.

11. CRC Handbook of Chemistry and Physics, Robert C. Weast, ed.; CRC Press, 1976-1977, 57th edition.

12. E. Furimski, Erdol and Kohle, 35, 445 (1982).

Table 1 - <u>Typical analysis of ilmenite ore</u>
<u>From St-Urbain deposits, Quebec</u>

Constituent	wt %
TiO_2	38.70
Fe_2O_3	18.64
FeO	28.66
SiO_2	4.27
Al_2O_3	4.00
MgO	4.80
CaO	0.50
MnO_2	0.12
Na_2O	0.05
V_2O_5	0.16
Cr_2O_5	0.08
NiO	0.10
CuO	0.04
BaO	0.01

Table 2 -   Typical Properties of Coker Kerosene

Boiling range	°C	193-279
Specific gravity	60/60°F	0.871
Sulphur	wt %	2.32
Nitrogen	ppm	430
Pour point	°F	Below -60
Cloud point	°F	Below -60
Flash point	°F	116
Vanadium	ppm	0.40
Nickel	ppm	0.36
Iron,	ppm	0.50
Ramsbottom Carbon Residue (10% bottoms)	wt %	0.29
Aromatics and olefins	vol %	58
Saturates	vol %	42

Table 3 - <u>Composition of standard solution</u>

Compound	ppm N
aniline	30.12
1,2,5-trimethylpyrrole	28.20
benzylamine	39.79
n-octylamine	32.62
quinoline	32.02
n-decylamine	27.08
indole	29.37
3-methylindole	26.74
$2,2^1$-dipyridyl	55.58
2-phenylpyridine	24.26
1-phenethylpiperidine	22.88
dibenzylamine	26.48
tetrahydrocarbazole	27.70
carbazole	25.24
2-methylacridine	19.40
3,4-benzacridine	7.85
2-aminochrysene	13.90
phenothiazine	29.60
Total N concentration	518.21

Table 4 - Order of breakthrough for model compounds

Curve from Fig. 2	Compound	Volume at which 10% is reached (mL)	PKa*	Proton Affinity**
1	Carbazole	1		
2	3-methylindole	20		
3	Phenothiazine	25		
4	Indole	31		
5	Tetrahydrocarbazole	30		
6	Aniline	45	4.63	213.5
7	2-phenylpyridine	45		
8	2-aminochrysene	45		
9	1,2,5-Trimethylpyrrole	48		
10	3,4-benzacridine	51		
11	n-octylamine	55	10.65	
12	n-decylamine	60	10.63	
13	Quinoline	65	4.90	228.4
14	2-methylacridine	100		
15	Benzylamine	100	9.33	
16	1-phenethylpiperidine	-		
17	2,2'-dipyridyl	-		
18	Dibenzylamine	-		

*Ref. 11
**Ref. 12

Table 5 - CLASSES OF COMPOUNDS BASED ON ADSORPTION BEHAVIOR

	Compound	Class	Basicity	Adsorption capacity	Reversibility
1.	carbazole	1	acidic	low	irreversible
2.	3-methylindole	1	acidic	low	irreversible
3.	Phenothiazine	1	acidic/neutral	low	irreversible
4.	Indole	1	acidic/neutral	low	irreversible
5.	Tetrahydrocarbazole	1	acidic/neutral	low	irreversible
6.	aniline	2	weak	medium	reversible
7.	2-phenylpyridine	2	weak	medium	reversible
10.	3,4-benzacridine	2	weak	medium	reversible
13.	Quinoline	2	weak	medium	reversible
14.	2-methylacridine	2	weak	medium/high	reversible
8.	2 aminochrysene	3	strong	high	-
9.	1,2,5 trimethylpyrrole	3	weak	medium/high	-
11.	n-octylamine	3	weak	medium/high	-
12.	n-decylamine	3	strong	medium/high	-
15.	Benzylamine	3	strong	very high	-
16.	1-phenetylpiperidine	4	strong	very high	-
17.	2,2^{1} Dipyridyl	4	strong	very high	-
18.	Dibenzylamine	4	strong	very high	-

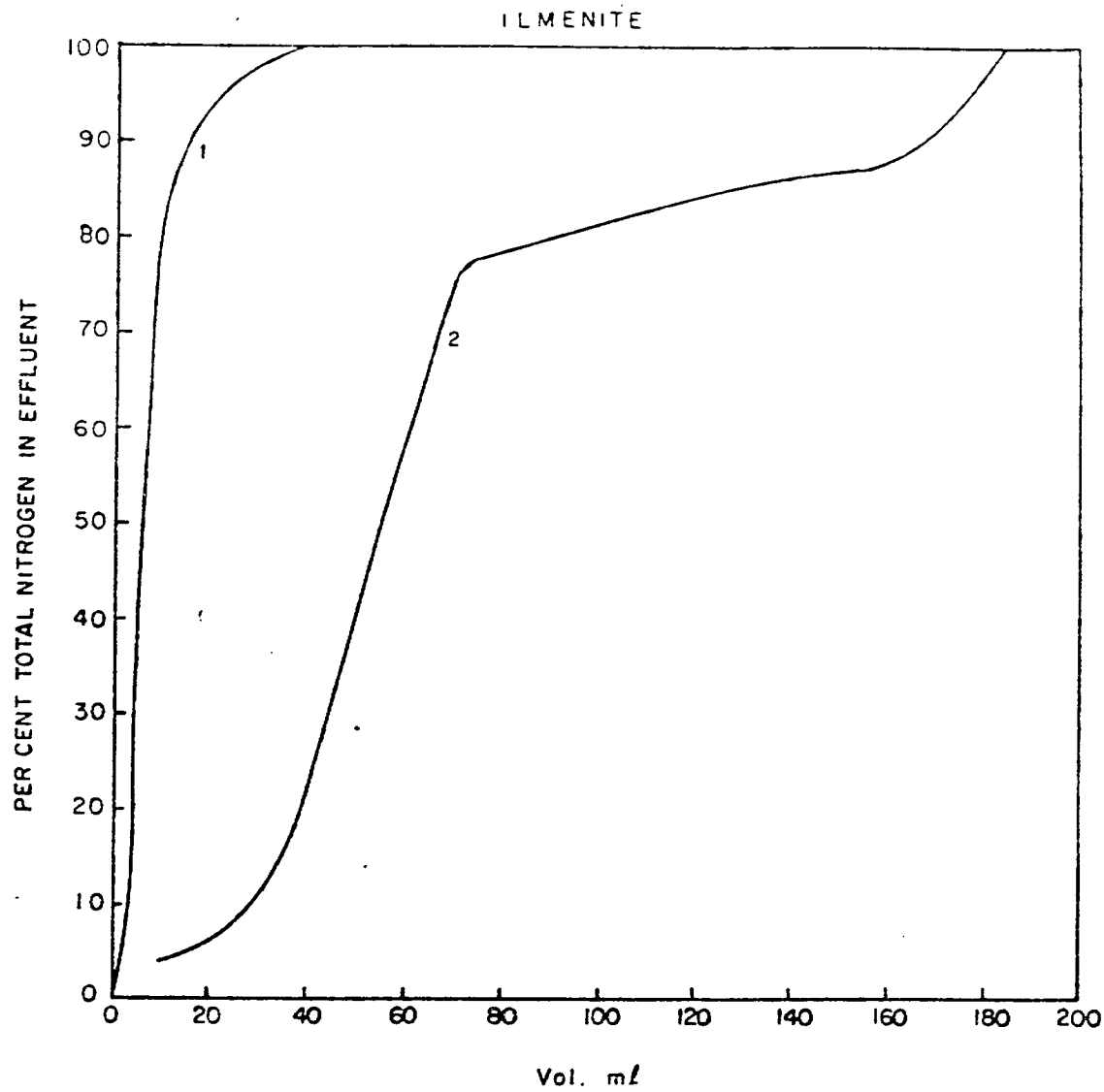Fig. 1 - Breakthrough curve for the adsorption of
nitrogenous compounds on 1) brominated ilmenite
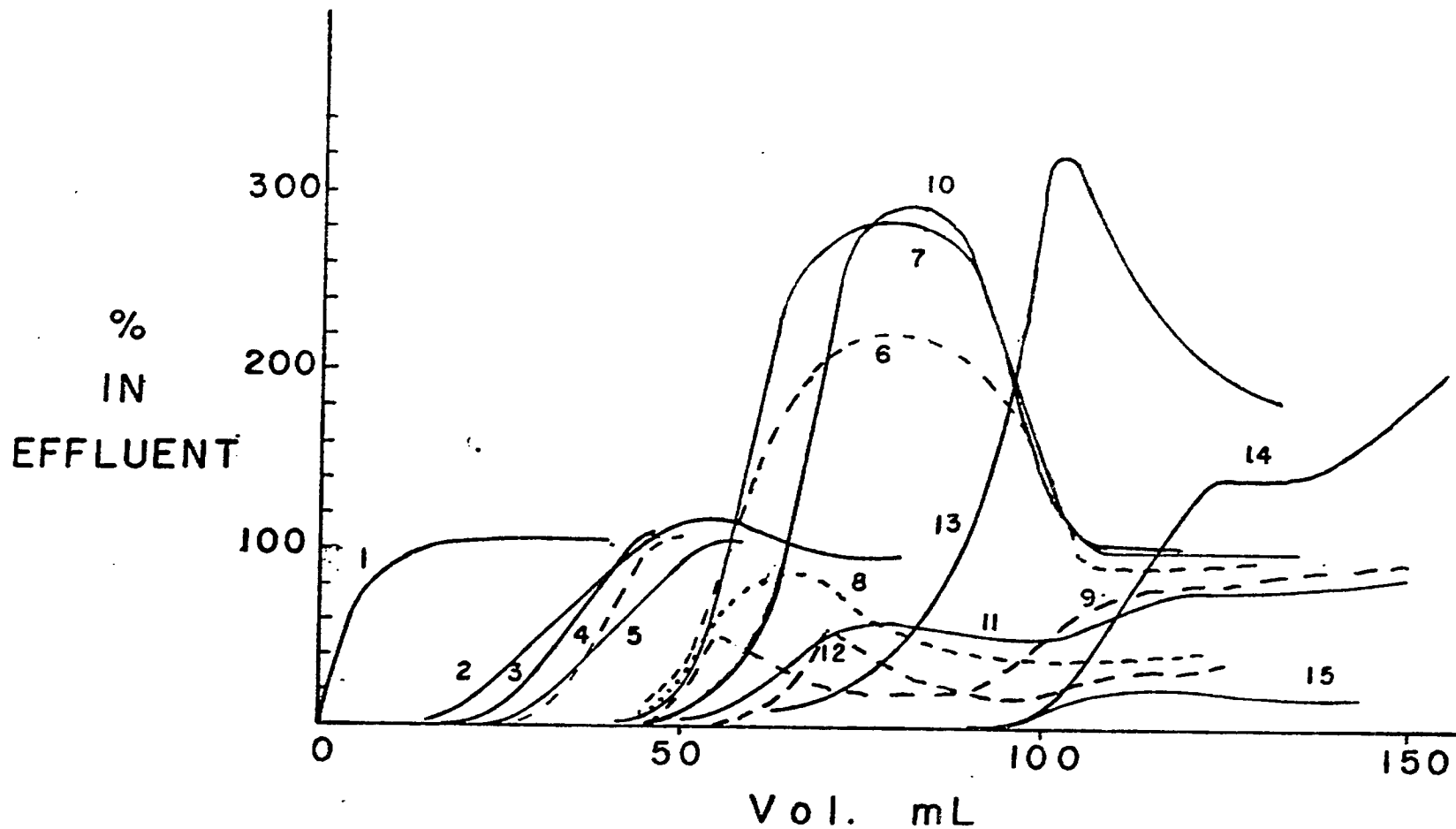washed with methanol; 2) brominated ilmenite

Fig. 2 – Breakthrough curves of individual compounds 1) carbazole; 2) 3-methylindole; 3) phenothiazine; 4) indole; 5) tetrahydrocarbazole; 6) aniline; 7) 2-phenylpyridine; 8) 2-aminochrysene; 9) 1,2,5-trimethylpyrrole; 10) 3,4-benzacridine; 11) n-octylamine; 12) n-decylamine; 13) quinoline; 14) 2-methylacridine; 15) benzylamine; not broken through: dibenzylamine; 1 phenetylpiperidine; 2,2' dipyridyl
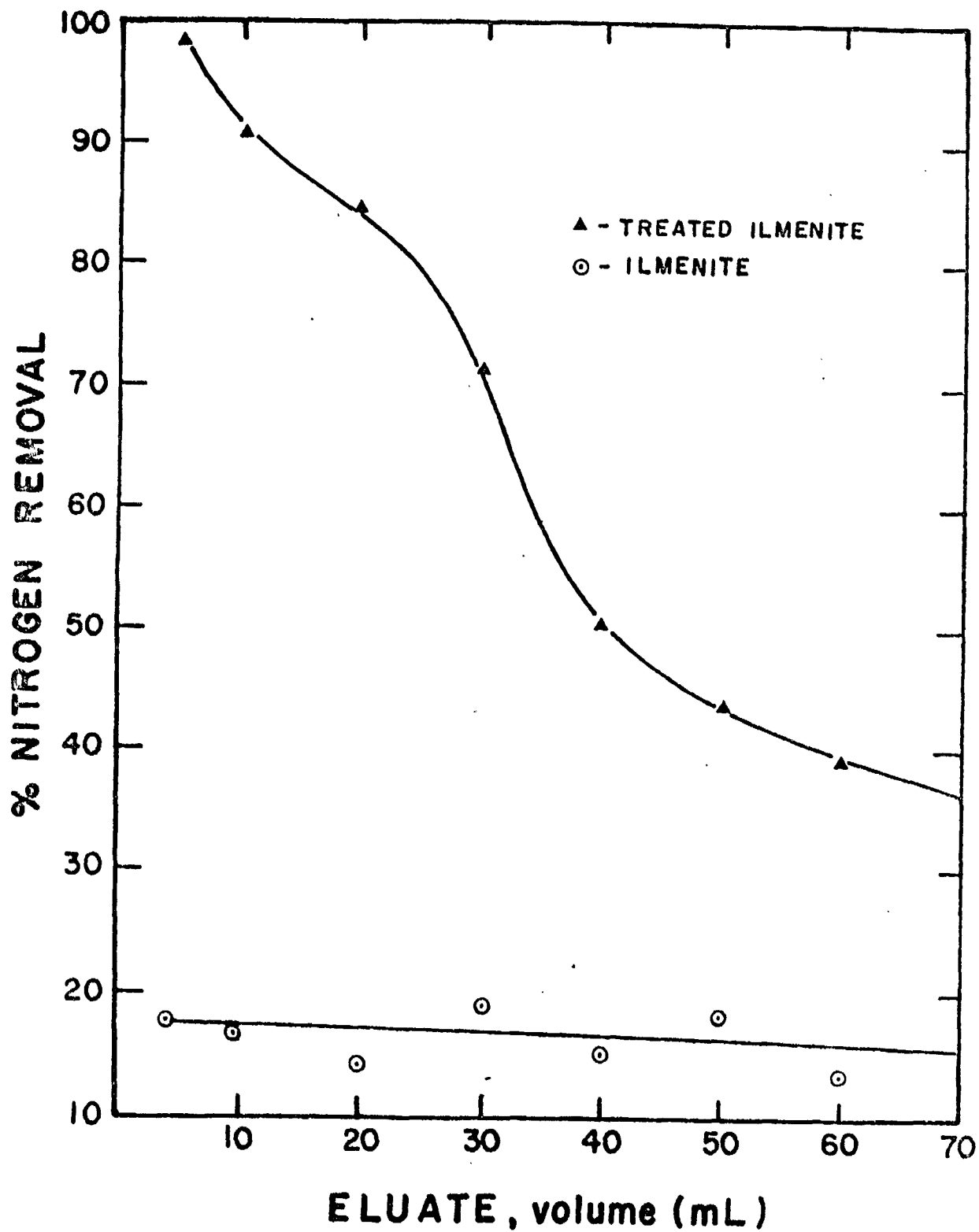
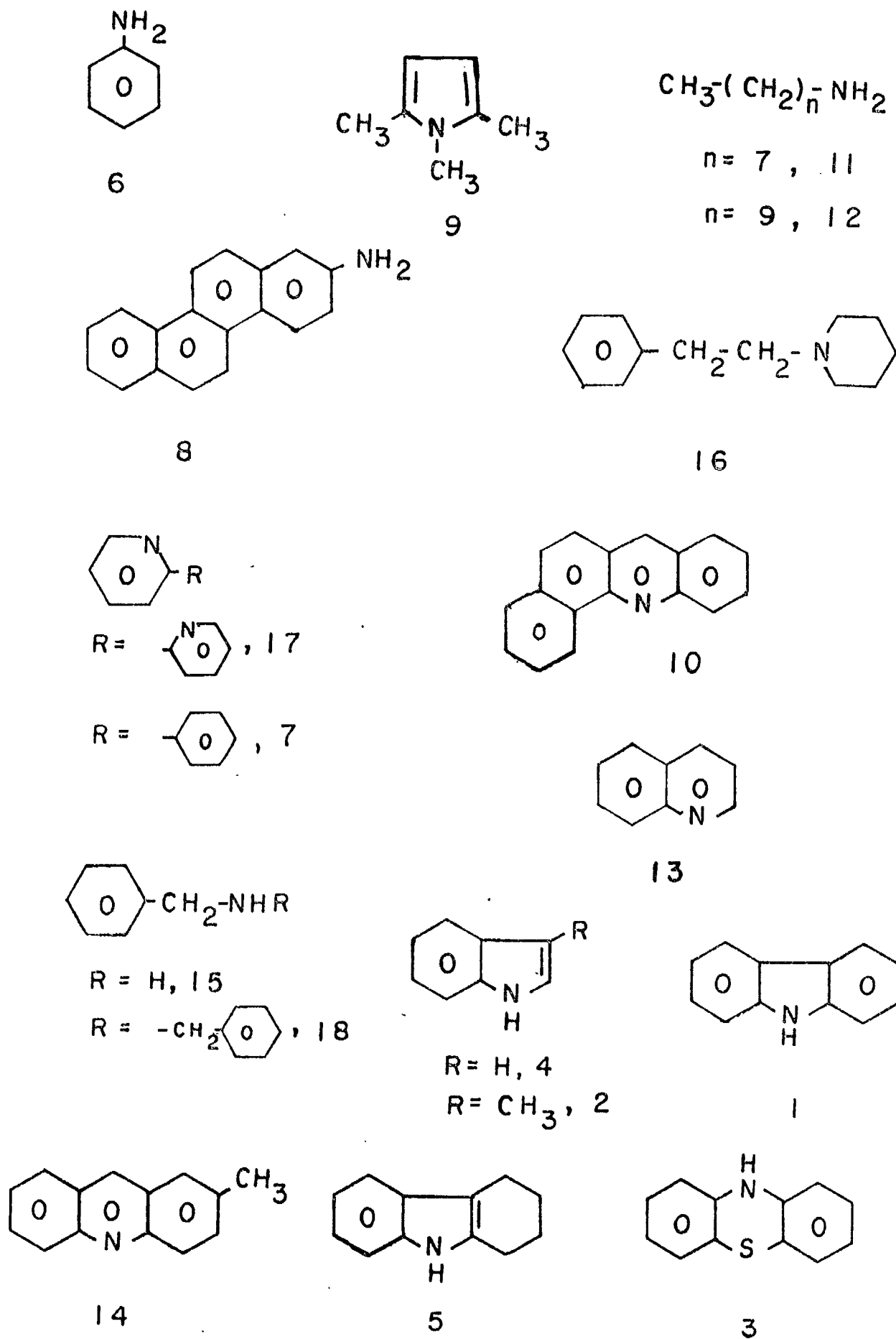Fig. 3 – Comparison of ilmenite with treated ilmenite for removing nitrogen from coker kerosene.

Fig. 4 — Structures