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## SELECTIVE SEPARATION OF "NONBASIC" NITROGEN COMPOUNDS FROM PETROLEUM BY ANION EXCHANGE OF FERRIC CHLORIDE COMPLEXES

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### SUMMARY

"Nonbasic" nitrogen compounds in petroleum products are quantitatively removed from hydrocarbons and other nonhydrocarbons by complex formation with ferric chloride supported on kaolin. The colored complexes remaining adsorbed on the kaolin are easily desorbed with 1,2-dichloroethane and other polar organic solvents. The free nitrogen compounds are quantitatively recovered by contacting a dichloroethane solution of the complexes with a strong anion exchange resin of the quaternary ammonium hydroxide type.

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### INTRODUCTION

The petroleum industry has been concerned for many years with the problem of isolating various types of nonhydrocarbon impurities from petroleum for purposes of identification. Although nitrogen compounds generally represent only a small percentage of these nonhydrocarbon constituents, they are among the most deleterious to refining catalysts and confer adverse stability properties. Numerous investigations have been made on the basic nitrogen compounds since they are readily accessible. The majority of nitrogen compounds, though, do not contain basic functional groups and consequently present greater problems in characterization studies. This paper briefly discusses techniques that are unique and useful in the separation of trace levels of "nonbasic" nitrogen compounds in a variety of petroleum products. The techniques include the independent use of coordination and ion exchange reaction chemistry. The study shows that nonbasic, as well as basic, nitrogen compounds present in petroleum are capable of forming isolable complexes with ferric chloride supported on clay mineral kaolin. The resulting complexes can be quantitatively

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cleaved by means of anion exchange resin chromatography to yield the original nitrogen compounds.

#### EXPERIMENTAL

Ferric chloride is supported on the clay mineral kaolin, 60–100 mesh, by stirring the latter with an equal volume of hot saturated methanolic ferric chloride hexahydrate for several minutes, followed by a rapid filtration. The cold filter cake is broken and washed with two portions of cold methanol (room temperature) to remove entrained nonadsorbed metal salt, and two additional washings are made with benzene to remove the methanol. The filter cake is then dried at 30° in a stirred air bath producing a light yellow powder containing approx. 2.2 % iron. The powder is easily used in conventional chromatographic column techniques.

TABLE I

EFFECT OF  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  ON NITROGEN CONTENT OF PETROLEUM

Sample	Pretreatment	Nitrogen, p.p.m.	
		Original	After reaction*
1 Kuwait heavy gas oil	None	810	280
2 Kuwait heavy gas oil	Bases removed	466	Trace
3 Wilmington heavy gas oil	Acids and bases removed	2000	Trace
4 Kuwait furnace oil	Bases removed	12	Trace
5 Texas transformer oil	Bases removed	19	Trace
6 Kuwait cracked naphtha	Bases removed	150	10

\* No basic nitrogen remains after each reaction as determined by titration with 0.1 *N* perchloric acid–glacial acetic acid.

Nitrogen compounds are removed by slowly percolating light petroleum distillates or hexane solutions of high-boiling petroleum fractions through beds of the synthetic adsorbent or by stirring the adsorbent with the distillate in successive portions and filtering (batch treatment); the former method is preferred. As the distillate reacts with the adsorbent, a rapid color change to green or blue occurs, indicating the formation of iron complexes on the surface of the kaolin. Entrained oil is removed from the adsorbent by exhaustive hexane elution. The effluent oils may be freed from traces of entrained colored complexes by contacting with a strong anion exchange resin.

The colored complexes of nitrogen compounds are desorbed from the kaolin by exhaustive elution with 1,2-dichloroethane. The solution of complexes is blue-green, exhibiting a broad adsorption band at 630  $m\mu$ . This solution is percolated through a bed of strong anion exchange resin (Amberlyst A-29)\* in the hydroxide form. The resin breaks the complexes as indicated by a loss of blue color and the disappearance of the 630  $m\mu$  band. The metal salt is retained on the resin while the free nitrogen compounds are recovered in resulting effluents.

\* Mention of specific products or brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

## RESULTS AND DISCUSSION

Table I shows some typical data obtained on different types of petroleum products that have been successfully denitrogenated by ferric chloride supported by kaolin. Except for sample No. 1, the nitrogen compounds in the original oils are only the neutral or nonbasic types, since basic compounds had been removed with mineral acids<sup>1</sup> or cation exchange resins<sup>2</sup> prior to treatment with ferric chloride. Removal of 92–100 % of "nonbasic" nitrogen is normally observed. Samples 1 and 2 are actually the same oil except the latter had been previously extracted with aqueous hydrochloric acid. The data show that 65.4 % of the total nitrogen could be removed in one experiment (sample 1) and essentially 100 % of the nitrogen was removed in a second experiment (sample 2). No basic nitrogen could be detected in the treated samples. These two experiments demonstrate that when basic nitrogen compounds are present in the oil they will be the type initially removed by ferric chloride; if total denitrogenation is desired, the oil must be contacted successively with fresh portions of the ferric chloride-kaolin adsorbent. Since basic nitrogen compounds are easily separated by mineral acids, most oils are pretreated in this manner to improve the overall efficiency of the ferric chloride-kaolin reagent; the neutral nitrogen compounds, as a class, are therefore more easily isolated by using the pretreated oils. Efficiency of nitrogen removal is also improved if acidic compounds are removed prior to treatment with ferric chloride-kaolin. Sample No. 3 in Table I is an example of large amounts of neutral nitrogen being removed when both acidic and basic constituents are previously removed. Complete removal of nitrogen compounds also could have been achieved without the prior removal of acids and bases, if selectivity for nonbasic types were not desired. Sample 6 seems to show a slight loss of efficiency of the reagent for severely cracked petroleum nitrogen compounds; a thorough study of these nitrogen compounds may provide an explanation for this observation. However, sample 6 could be completely denitrogenated with excess reagent.

Because ferric chloride will react in differing stoichiometries with different nitrogen functional groups (and phenols), one cannot precalculate the exact amount of reagent for any given type of oil. The fact that some reactive sites are not actually in positions suitable for a surface reaction with nitrogen donor groups is a further point for consideration. Numerous experiments in these laboratories indicate that when the ratio of pretreated oil to adsorbent is 1:2 (by weight), all "neutral" nitrogen compounds could be removed even if the nitrogen content is as high as 0.2 %, as shown in sample No. 3, Table I. The data in Table I were obtained by using a 1:2 ratio of oil to reagent.

The ferric chloride-kaolin technique is an improvement over the original approach to forming metal complexes of petroleum nitrogen compounds<sup>3</sup>. The present technique provides a means of isolating the nitrogen compounds from the hydrocarbons and heterocyclic oxygen and sulfur compounds; all of the latter types that are known to be present in petroleum are unreactive to the reagent. The kaolin can be coated with numerous transition metal salts in a manner similar to that described for ferric chloride if other types of complexes are desired; this may be useful where selectivity in removing certain types of nitrogen compounds is desired. Experiments in these laboratories have shown, though, that ferric chloride is the reagent of choice where complete denitrogenation of an oil is desired. After removing the complexes

from the kaolin with appropriate polar solvents, the kaolin may be reactivated and coated with additional metal salt.

Quantitative recovery of the original nitrogen compounds from their ferric chloride complexes is best achieved by using a strong anion exchange resin of the quaternary ammonium hydroxide type; these complexes could also be decomposed by heating<sup>3</sup> or by purging with ammonia or hydrogen sulfide<sup>4</sup>. MAYER's complexes of alkaloids have previously been decomposed on anion exchange resins to yield the free alkaloid<sup>5</sup>. This technique of recovering the free nitrogen compounds is very rapid and quite desirable, since these compounds are most stable in the basic environment. Also, small quantities of the resin are sufficient for large quantities of the complexes since the resin possesses a high capacity for the ferric ion. If desired, the resin can also be regenerated for re-use by standard techniques.

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