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Progress Report

REMOVAL OF NICKEL AND VANADIUM FROM PETROLEUM PRODUCTS

R. C. Elderfield
Supervisor

A. Hampton
Research Associate

UMRI Project 2165

ESSO RESEARCH AND ENGINEERING COMPANY
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ABSTRACT

     1. Dilute solutions of hypochlorous acid at about pH 6 remove a large part of the nickel from representative gas oil and a smaller part of the vanadium and iron.

     2. Substantial removal of nickel from so-called "secondary condensate" was also accomplished by hypochlorous acid treatment.

     3. Removal of both nickel and vanadium from representative crude oils was variable.

     4. A model synthetic vanadium porphyrin has been prepared for the first time.

OBJECTIVE

    The occurrence of small but significant percentages of trace metals, chiefly vanadium, nickel, and iron, in various petroleum products is a source of considerable concern to the oil industry. At the time the present investigation was undertaken, no completely satisfactory process for removal of these metal contaminants was at hand. A study of possible procedures for removal of such contaminants was therefore initiated.

DISCUSSION

INTRODUCTION

It is known that at least part of the vanadium present in certain crude oils occurs as soluble coordination complexes with porphyrins,[1,2,3] and in one instance the occurrence of a nickel porphyrin has also been reported.[4] Although the proportion of the total nickel and vanadium in petroleum which is actually combined with prophyrins is unknown, one approach to the problem of removing these metals involves an investigation of methods for their removal from synthetic porphyrin complexes and subsequent application of such methods to selected petroleum fractions. This approach was adopted in the present work. This report will therefore be divided into two parts: (A) attempts to remove nickel or vanadium from synthetic porphyrin complexes, and (B) processing of selected oil stocks.

A. EXPERIMENTS USING SYNTHETIC METALLO-PORPHYRIN COMPLEXES

1. Preparation of the Complexes

Porphyrins occurring in oil deposits appear to be largely decarboxylated,[1,2] but such types are not readily synthesized or separable in pure form from the natural source. Accordingly, the dimethyl ester of mesoporphyrin (I), which is conveniently prepared from hemin[5] and is an oil-soluble porphyrin, was selected as a model substance.
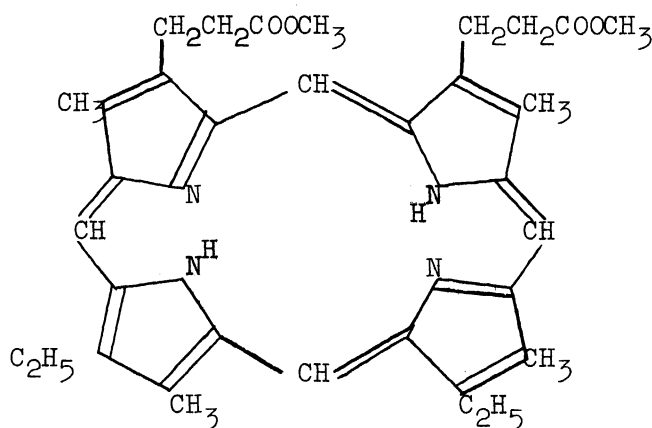
I

The nickel complex of I was made by the action of nickelous acetate in glacial acetic acid on I.[6] Attempts to prepare the corresponding vanadyl complex by heating I with vanadium tetrachloride and sodium acetate in acetic acid according to the procedure to Treibs[2a] were unsuccessful. However, the solubility of vanadyl acetate in acetic acid is increased by the addition of sodium acetate whereas the solubility of I is decreased. It was found that by heating vanadyl acetate and I with suitable quantities of acetic acid and sodium acetate, both reactants could be kept in solution and a satisfactory yield of the desired complex was obtained. A convenient source of vanadyl acetate is found in vanadyl chloride added directly to the reaction mixtures. Since the vanadyl complex melted at 248° and the complex of Treibs is reported to have no melting point, elementary analyses were done to confirm the structure. The two products were spectroscopically similar.

2. Action of Chelating Agents

Because of the unique configuration and extremely high stability of many porphyrin-metal complexes, direct removal of either nickel or vanadium with known chelating agents cannot be expected to occur readily. Two attempts along these lines were made. The first involved use of o-phenanthroline, since this represents an example of an oil-soluble agent which forms water-soluble complexes. However, spectrographic measurements showed that it was without effect on nickel mesoporphyrin dimethyl ester in light petroleum at 100°. The possible conversion of the porphyrin complex to a nickel phthalocyanine complex was also examined since it seems probable that metal complexes of certain of the phthalocyanines are less volatile than the corresponding porphyrin complexes.[8] However, no metal interchange occurred when phthalocyanine was heated at 200° in chloronaphthalene or quinoline with the nickel mesoporphyrin complex.

3. Ring Fission Attempts

A study was made of conditions under which the porphyrin ring system might be broken at one or more points to furnish polypyrrole fragments lacking the strong metal-binding power of the original porphyrin.

a. Hydroxylamine.—This reagent, which has been shown to rupture the pyrrole ring in alcoholic solution,[9] did not attack the nickel-porphyrin complex after 10 hr in boiling amyl alcohol.

b. Chlorinating Agents.—Sulfuryl chloride, which readily chlorinates 1-methyl groups in pyrrole[10] was found to convert solutions of the nickel-porphyrin in carbon tetrachloride or light petroleum at room temperature to a green, soluble pigment from which the nickel could be removed by shaking with dilute acid. Prior addition of a small amount of acetic acid gave rise to a red-brown solution, and nickel ions were again found in the aqueous washings of this solution. Trichloroacetic acid, which may be present under the latter conditions, had no action on solutions of the porphyrin complex in petroleum ether even at 100°.

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Similar results were obtained when gaseous chlorine was substituted for sulfuryl chloride. A milder chlorinating agent, N-chloroacetanilide, when boiled for several minutes with the nickel porphyrin, produced a green pigment from which nickel was removed by washing with dilute acetic acid. In carbon tetrachloride the reaction appeared to take a different course and no nickel could be removed by washing the acid.

When solutions of the nickel or vanadium porphyrins in organic solvents were shaken with solutions of bleaching powder in dilute hydrochloric acid, decolorization occurred and the metals passed into the aqueous phase. Aqueous hypochlorous acid containing no free chlorine had the same action, but solutions of bleaching powder in water or dilute alkali were inactive. Hypobromous, but not hypoiodous acid, was also effective.

The activity of hypochlorite solution decreased markedly above pH 8, and it appears likely that the agent attacking the porphyrin nucleus at pH 3 to pH 8 is probably undissociated hypochlorous acid rather than the hypochlorite anion or free chlorine since the pK_a of hypochlorous acid is 7.45 and the equilibrium

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$
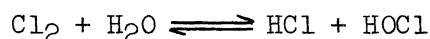
favors HOCl above pH 3.[11]

The vanadium complex was more resistant than the nickel complex and required a four-fold greater concentration of hypochlorous acid for an equivalent rate of attack.

c. <u>Coupled Oxidation</u>.—The known coupled oxidation of hemin to biliverdin by hydrogen peroxide and hydrazine in pyridine[12] suggested the possiblity of converting the nickel and vanadium porphyrins to mesobiliverdin dimethyl ester by a similar reaction. When air was passed through a pyridine solution of the vanadium complex containing hydrazine, or when hydrogen peroxide was added to the mixture, the red complex was changed to a yellow-green pigment. Quantities of the vanadium complex were at the time insufficient to determine whether vanadium could be removed by dilute acids.

The nickel complex, on the other hand, was unchanged by the coupled oxidation treatment. In addition, the reaction did not occur with the vanadium complex when kerosene was used as a diluent. In view of the limited scope of the reaction and practical difficulties in the way of applying it to petroleum samples, further work along this line was not pursued.

B. TREATMENT OF PETROLEUM STOCKS

1. Sulfuryl Chloride

West Texas residuum (containing 80 ppm of nickel and 180 ppm of vanadium) was diluted with kerosene and treated at room temperature with 25% of its weight

of sulfuryl chloride. Extraction of the mixture with water and analysis of the treated residuum showed that no reduction in nickel or vanadium content had been achieved.

Negative results were also obtained when Tia Juana medium crude (19 ppm of nickel and 180 ppm of vanadium) was diluted with benzene and treated with 10% of its weight of sulfuryl chloride. These failures are probably due to the readiness with which the reagent attacked constitutents of the oils other than porphyrins.

2. Hypochlorous Acid

Preliminary experiments were done with West Texas crude and solutions of bleaching powder in hydrochloric acid at pH 6-7 to determine the effect of the initial amount and concentrations of hypochlorous acid on the loss of free chlorine from the aqueous solution. Other factors involved were light intensity during agitation, and duration of the agitation period.

A solution of the nickel mesoporphyrin dimethyl ester in West Texas crude was extracted with hypochlorous acid. Appreciable amounts of the added nickel were detected in the aqueous phase and the loss of free chlorine amounted to 4% of the weight of the oil used.

A solution of Bachaquero residuum (98 ppm nickel and 540 ppm of vanadium) in benzene was treated similarly with bleaching powder. No nickel and only a trace of vanadium were detected in the aqueous washings.

To facilitate the quantitative estimation of nickel and vanadium in the aqueous washings, subsequent experiments were carried out with solutions of hypochlorous acid prepared by passage of chlorine into sodium carbonate solution. The results of six typical runs are given in Table I.

These results indicate that the process can remove most or all of the nickel present in high-boiling distillates, but it is less effective with crude oils, and relatively ineffective with residua. Such variations must parallel to some extent the concentration of nickel-porphyrin complex in the samples, and they provide an estimate of the maximum percentage of the total nickel present as a simple porphyrin complex. Thus, while most of the nickel in the oil distillates may be in the form of a complex, no more than 20% of the nickel in Tia Juana medium crude appears to be bound to simple porphyrins and little or no nickel porphyrin occurs in Bachaquero residuum. As judged by this criterion, residua contain relatively small amounts of nickel or vanadium porphyrins, presumably because of volatilization and thermal decomposition of these substances during distillation. The inability of hypochlorous acid to extract appreciable quantities of nickel from residua is understandable from the fact that it has very little metal-removing action on heat-soaked nickel porphyrin complex (see below).

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TABLE I

TREATMENT OF OIL STOCKS WITH HYPOCHLOROUS ACID

Stock	Metal Content (ppm)*		Removal of Metals (%)**		Loss of Cl_2 from Water (g Cl_2/100 g oil)
	Ni	V	Ni	V	
So. La. Gas Oil (ELLA-686)	2.3	0.3	75	0	2.9
Secondary Condensate (from ERE Process Div.)	0.15	3.7	80-100	0	1.55
Tia Juana Medium Crude	19.0	180.0	19	22	4.9
Bachaquero Whole Crude	3.85	7.2	144	950***	10.0
So. La. Residuum	8.5	0.55	13	0	3.9
Deasphalted Oil From Baytown 1954 Feed*	0.9	0.6	72	0	4.0

*Metal content of original stock is from data supplied by either ERE Process Research Division or ESSO Laboratories (Louisiana Division).
**Determined by analysis of water wash.
***These figures are being checked at Baton Rouge.

The successful removal of vanadium was demonstrated only with Tia Juana and Bachaquero crudes. However, addition of known amounts of vanadyl chloride to the aqueous hypochlorous acid before treatment of an oil sample showed that the procedure used for estimation of vanadium gives low values, and, in fact, would not reveal an amount of this metal corresponding to the complete removal of at least 2 ppm from the samples. Three of the stocks listed in Table I contain less than 2 ppm of vanadium. The actual amount of vanadium removed from these is being determined by direct analysis of the treated stocks. The data are not presently available.

The extent of chlorination of stocks treated with hypochlorous acid was examined by chlorine analyses of the treated stocks in the cases of Bachaquero crude and deasphalted oil from Baytown 1954 feed. Results are given in Table II.

Since no precautions were taken to exclude light, not much weight is placed on these figures (Table II).

LOCATION:

SERIES   yes / (no)

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2. Access point searched: A   HAMPTON

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2.

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Item 2

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TABLE II

CHLORINE CONTENT OF UNTREATED AND HYPOCHLORITE-TREATED STOCKS

Stock	Cl Content (%) Before Treat	After Treat
Bachaquero crude	trace	3.53
Deasphalted oil from Baytown 1954 feed	none	1.52

C. THERMAL STABILITY OF PORPHYRIN COMPLEXES

In view of the observation made elsewhere that heat soaking apparently reduces the metal porphyrin content of oils,[13] a few experiments on the effect of heat soaking on the synthetic porphyrin were done. Spectrographic assay showed that after heating in paraffin wax at 370-390°C for 6 hr, 30% of the nickel complex and 16% of the vanadium complex were decomposed. The amount of nickel removed by hypochlorous acid treatment was simultaneously reduced from 99% to 85%.

EXPERIMENTAL

NICKEL MESOPORPHYRIN DIMETHYL ESTER

A mixture of mesoporphyrin dimethyl ester (0.72 g) prepared from 1.9 g of hemin according to Corwin and Erdman,[5] nickelous acetate (2.0 g), and glacial acetic acid (30 ml) was refluxed for 2 hr. When cool, the crystalline suspension was poured into water and the red precipitate was collected and dried in vacuo. Recrystallization by concentration of a solution of the complex in 25 ml of acetic acid to 15 ml gave 0.7 g of red needles, mp 192°. The complex showed the following spectrographic behavior in dioxane: λ_{max}: 517 and 551 mμ; $\epsilon_{517}/\epsilon_{551}$: 0.37. Reported[7] λ_{max}: 514 and 550 mμ; $\epsilon_{514}/\epsilon_{551}$: 0.34.

VANADYL MESOPORPHYRIN DIMETHYL ESTER

Anhydrous sodium acetate (25 g) was added at 90° to a solution of mesoporphyrin dimethyl ester (1.0 g) in acetic acid (150 ml). When most of the solid had dissolved, vanadyl chloride (4 g) was added at about 60° and the mixture was refluxed for 7 hr in a bath at 165-170°. The cooled mixture was poured into

1000 ml of water and the red solid was collected, washed thoroughly with water, and dried in vacuo over potassium hydroxide. The product was triturated under 150 ml of cold chloroform, and the soluble portion, after removal of the solvent, was dissolved in 300 ml of benzene. The solution was passed through a column (4.5 x 25 cm) containing 450 g of precipitated calcium carbonate. The column was washed with benzene and the combined benzene effluents were evaporated to dryness. A solution of the residual solid in 100 ml of chloroform was passed through a column (2.2 x 6 cm) of alumina and the column was washed free of red pigment with chloroform. A strongly adsorbed dark red zone remained on the alumina. The solution was evaporated and the residue (0.8 g, mp 240-242°) was recrystallized three times from acetic acid (8 parts) and twice from chloroform (15 ml) to which hot methanol (150 ml) had been added. Red needles (0.55 g), mp 248°, were obtained.

Anal. Calcd. for $C_{36}H_{40}N_4O_5V$: C, 65.54; H, 6.11; N, 8.49; OCH_3, 9.41; V, 7.72.

Found: C, 65.68; H, 6.29; N, 8.70; OCH_3, 9.25; V, 7.71.

The complex showed the following spectrographic bevahior in dioxane. λ_{max}: 321, 406, 502, 535, 571 mμ; log ϵ: 4.32, 5.45, 3.33, 4.16, 4.39, respectively. Reported[7]: λ_{max}: 500, 533, 570 mμ; log ϵ: 3.37, 4.17, 4.42, respectively.

ACTION OF CHELATING AGENTS ON THE COMPLEXES

1. o-Phenanthroline

A saturated (20°) solution of the nickel complex in light petroleum (20 ml; bp 90-100°) was refluxed for one hour with o-phenanthroline hydrate (10 mg), cooled, and extracted with four 20-ml portions of N hydrochloric acid. A control solution was made by extracting the saturated solution of nickel complex once with N hydrochloric acid without treatment with o-phenanthroline. Both solutions were diluted with half their volume of petroleum and examined spectrographically in 1-cm cells in the region 500-600 mμ.

Untreated solution: λ_{max}: 517 mμ, D: 0.196; λ_{max}: 552 mμ, D: 0.665.

Treated Solution: λ_{max}: 517 mμ, D: 0.196; λ_{max}: 552 mμ, D: 0.662.

2. Phthalocyanine

Nickel porphyrin (1 mg) was added to a saturated solution of phthalocyanine prepared according to Linstead and Lowe[14] in quinoline (20 ml) and the solution was heated at 200° for one hour. Before heating, the solution had absorption maxima at 518, 553, mμ (porphyrin complex peaks), and at 603, 640, 670, and 700 mμ (phthalocyanine peaks), density values being 0.275, 0.795, 0.745, 1.08, 1.98, and 1.98, respectively. After heating, the absorption peaks were unaltered and the density values were 0.237, 0.638, 0.632, 0.910, 1.92, and 1.97. Within

the limit of accuracy of these readings, no evidence could be found for the appearance of a new peak at 676 mμ corresponding to the strongest absorption region of nickel phthalocyanine.

In a similar experiment in which chloronaphthalene was substituted for quinoline, and heating at 180° was for 3 hr, the results were similar to the above.

RING FISSION ATTEMPTS

1. Hydroxylamine

A portion of a solution of the nickel porphyrin (1 mg), hydroxylamine hydrochloride (1 g) and sodium carbonate monohydrate (0.7 g) in 20 ml of n-amyl alcohol was refluxed for 10 hr. No difference in absorption maxima at 515 and 551 mμ was found in the heated and unheated solutions.

2. Chlorinating Agents

a. Sulfuryl chloride.—Sulfuryl chloride (0.15 ml) was added to a solution of the nickel porphyrin (2 mg) in 20 ml of carbon tetrachloride. After standing for 30 min, the green solution was extracted with 5% hydrochloric acid. After concentration of the acid wash to 5 ml the characteristic nickel salt of dimethylglyoxime was formed on addition of the reagent at pH 7. The carbon tetrachloride solution was washed with water, dried, and taken to dryness. The residual dark green solid in dioxane had absorption maxima at 451 and 585 mμ. It did not give the zinc acetate-sodium test for mesobilatriene, nor was it similar to mesobiliverdin (λ_{max}: 290, 313 mμ in dioxane).

When acetic acid (0.1 ml) was added with or before the sulfuryl chloride, a red-brown solution resulted. When shaken with water, a green pigment, soluble in carbon tetrachloride and insoluble in water, was formed. The absorption curve at 350-700 mμ was similar to that of the green pigment obtained in the absence of acetic acid although the peaks were shifted about 10 mμ toward the shorter wavelengths. Nickel was detected in the aqueous washings with dimethylglyoxime.

Substitution of trichloroacetic acid for acetic acid led to a similar reaction, but when the nickel porphyrin was refluxed (90-100°) in light petroleum containing trichloroacetic acid for 2 hr, no reaction occurred.

b. Chlorine.—A hot saturated solution of the nickel porphyrin in light petroleum (bp 90-100°) was cooled rapidly to 20° and a slow stream of chlorine was passed through it for several minutes. The red solution immediately became yellow and a tan precipitate formed. The mixture was kept at 20° for one hour and the excess chlorine was removed in a current of air. The suspension was extracted with 5% hydrochloric acid. The aqueous layer contained nickel. The

petroleum solution, which became green during the extraction, was evaporated to dryness. The residue had absorption peaks at 451 and 585 mμ in dioxane.

When chlorine was bubbled for 5 min into a solution of the nickel complex (2 mg) in 20 ml of carbon tetrachloride containing trichloroacetic acid (0.1 g), the mixture initially became darker red but finally was orange. Extraction with 10 ml of water removed nickel ions and left a green carbon tetrachloride solution.

c. N-Chloroacetanilide.—A solution of N-chloroacetanilide (20 mg) and nickel porphyrin (2 mg) in 20 ml of chloroform was heated for 10 min on the steam bath. The mixture became green during the first minute of heating. Acetic acid (1 ml) was added and the resulting brown solution was washed with water. Nickel ions were detected in the washings with dimethylglyoxime.

When carbon tetrachloride was substituted for chloroform, only a slight deepening of color was noticeable even after boiling for 15 min, and no nickel could be removed with dilute acetic acid. When hot kerosene was the solvent a green pigment formed immediately. The reason for this variable behavior was not investigated further.

Solutions of the vanadyl porphyrin in chloroform gave a brown pigment after heating for 5 min.

d. Hypochlorous Acid.—Solutions of the nickel and vanadyl porphyrins in chloroform, carbon tetrachloride, and light petroleum behaved alike toward bleaching powder solutions in the following experiments. Solutions of bleaching powder in water or in sodium hydroxide solutions had no effect on the complexes, but in the presence of a trace of acid, rapid decolorization occurred and metallic ions were released into the water. (Unless otherwise indicated, the detection and estimation of nickel and vanadium were performed with dimethylglyoxime and diphenylbenzidine, respectively, according to the procedures given in ESSO Research Center Memorandum No. 79.) The use of sufficiently dilute solutions of bleaching powder showed that in the case of the vanadyl complex, the reaction occurred through the intermediate formation of a green pigment which required approximately four times as much bleaching solution as the nickel complex for the same rate of decolorization.

Determinations of pH with a glass electrode revealed that appreciable activity was retained from strongly acidic regions to pH 8. A solution of hypochlorous acid freed from chlorine by shaking chlorine water for several hours with excess mercuric oxide was found to be equally effective as was hypobromous acid prepared similarly. Hypoiodous acid had no effect on either the nickel or vanadyl complex. When a solution of hypochlorous acid prepared as above was extracted with carbon tetrachloride and the dried (sodium sulfate) extract was added to a solution of nickel porphyrin in the same solvent, a color change from pink to greenish-yellow was observed. This color persisted for several days unless a wet solution of hypochlorous acid in carbon tetrachloride was used. Decolorization of the green pigment then occurred in 30 min.

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3. Coupled Oxidation

a. Hydrogen peroxide (1 ml of 3% solution) and hydrazine hydrate (0.1 ml freshly distilled) were added to a solution of the vanadyl complex in pyridine (1 ml). The red solution on warming produced a green froth, and when aerated at room temperature for 30 min, the bulk of the solution turned dark green.

b. The above experiment was repeated omitting the hydrogen peroxide and aerating the mixture at about 90° (steam bath). The solution became brown-green after 10 min and yellow after 45 min. More pyridine (0.5 ml) and hydrazine (0.1 ml) were added and aeration was continued at 90° for one hour. No further change occurred. The solvent was evaporated on the steam bath and the brown residue was dissolved in methanol-hydrochloric acid (10:1). The solution had only one absorption peak in the range 340-680 mμ, located at 360 $\pm$ 5 mμ, and hence contained little or no mesobiliverdin (λ_{max}: 670, 363, and 309 mμ).

c. Hydrazine hydrate (0.1 ml) was added to a solution of the vanadyl complex (1 mg) in kerosene (5 ml) containing pyridine (0.5 ml) and the mixture was heated on the steam bath and aerated for 2 hr. The red color of the solution remained unchanged. The sparing solubility of the hydrazine in the mixture may account for the result.

d. When the nickel complex was treated as in b above, no color change was observed.

e. Mesoporphyrin dimethyl ester was also unchanged under the conditions of experiment b above.

4. Thermal Stability of the Porphyrin Complexes

Stock solutions of nickel complex (25 mg) and vanadyl complex (20 mg) each in chloroform (50 ml) were prepared. Exactly 5 ml of each solution was evaporated to dryness in the same 100-ml flask. The residue was dissolved in warm Parowax (20 g) and this solution was heated at 370-390°C for 6 hr. The resulting mixture was diluted with benzene to 100 ml in a volumetric flask. The experiment was re-peated using Parowax alone to obtain a blank solution for spectrophotometric meas-urements.

A mixture of 5 ml of each of the stock solutions was diluted to 200 ml with benzene and the spectrum of this solution was taken in a 1-cm cell. Maxima at 553 mμ (D = 0.720) (due to the nickel complex) and at 571 mμ (D = 0.522) (due to the vanadyl complex) were observed.

The benzene solution of the heated complexes was diluted with an equal vol-ume of benzene and the following readings taken: D_{553} = 0.500; D_{571} = 0.436. Thus at least 30% of the nickel complex and 16.5% of the vanadyl complex had been destroyed by heating at the above temperature.

A solution of hypochlorous acid was prepared by passing chlorine into a so-lution of sodium carbonate monohydrate (0.61 g) in 100 ml of water until 5 ml of

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the solution after treatment with potassium iodide was equivalent to 5.5 ml of 0.1 N sodium thiosulfate. A solution of nickel complex (2.5 mg, from 5 ml of stock solution) and vanadyl complex (2.0 mg, from 5 ml of stock solution) in benzene (100 ml) was shaken for 2 min with 50 ml of the hypochlorous acid solution and 250 ml of water. The aqueous layer was separated and extracted with benzene (50 ml) and the combined benzene extracts were shaken with two 50-ml portions of 0.01 N hydrochloric acid. The combined aqueous solutions were evaporated to dryness and the residue was taken to dryness twice with 10-ml portions of 5 N hydrochloric acid. Assay of the residual solid indicated that 98.7% of the total nickel and 40% of the total vanadium had been removed from the benzene solution by the hypochlorous acid treatment. When the heat-soaked complexes were treated similarly with hypochlorous acid, 85% of the nickel and 62% of the vanadium were extracted.

A check on the accuracy of the vanadium estimation (by the diphenylbenzidine method) was made by adding 150 γ of vanadium to the same amount of hypochlorous acid solution as was used in the above extractions and evaporating the mixture to dryness as above. The assay for vanadium was found to be 15% low, and hence the results obtained above regarding removal of vanadium by hypochlorous acid cannot be considered to be reliable.

TREATMENT OF OIL SAMPLES

1. Sulfuryl Chloride

West Texas residuum (20 g) dissolved in kerosene (bp. 180-240°) (250 ml) was treated with sulfuryl chloride (5 ml) and trichloroacetic acid (2 g) at room temperature. Sulfur dioxide was liberated, the mixture became warm and a dark orange sludge precipitated. After standing for one hour, the mixture was shaken with 200 ml of water, and the resulting emulsion was separated by centrifuging. The kerosene solution was extracted with 200 ml of N hydrochloric acid and the mixture was centrifuged after addition of 20 g of sodium sulfate. Analysis of the oil after removal of kerosene showed no reductions in nickel or vanadium content.

Tia Juana medium crude (50 g) in benzene (150 ml) was treated with sulfuryl chloride (5 ml) and acetic acid (2 ml) for one hour. After extraction with one liter of water and one liter of 0.1 N hydrochloric acid, analysis of the aqueous extracts showed no detectable amounts of nickel or vanadium.

2. Hypochlorous Acid

Two examples are given to illustrate the effect of the initial concentration of hypochlorous acid on shaking with an oil sample. The pH of the solution used was 7.3.

a. Bleaching powder (1.26 g) was dissolved in 200 ml of 0.05 N hydrochloric acid. After treatment with potassium iodide and acetic acid, 10 ml of this solution consumed 10.4 ml of 0.1 N thiosulfate. West Texas crude (5 ml) was shaken.

for 2 min with 180 ml of this solution and 180 ml of water. Titration of 10 ml of the aqueous phase consumed 2.7 ml of 0.1 N thiosulfate. Hence the chlorine content of the hypochlorous acid solution had decreased by 0.315 g. It should be pointed out that at least part of the chlorine loss is undoubtedly due to sweetening of the originally sour stock.

b. Experiment a was repeated using only 45 ml of hypochlorous acid solution and 315 ml of water. The chlorine loss was 0.107 g. The aqueous phase when shaken with a solution of the nickel complex in carbon tetrachloride accomplished complete decolorization in 2 min.

c. A solution of the nickel complex (3 mg) in West Texas crude (10 ml) was shaken with 180 ml of the above hypochlorous acid solution and 540 ml of water. The concentrated aqueous extract gives a strongly positive test for nickel with dimethylglyoxime.

d. For treatment of the oil samples listed in Table I (p. 5), solutions of hypochlorous acid of pH 6.6 were prepared by dissolving chlorine in a solution of 6.1 g of sodium carbonate monohydrate in 1000 ml of water until 5 ml of the solution liberated iodine equivalent to 5.4 ml of 0.1 N sodium thiosulfate. In most cases, 50-g samples of oil (in benzene solution) were shaken for 2 min with 1000 ml of the above hypochlorous acid solution and 3000 ml of water, although variations were occasionally required because of excessive loss of hypochlorous acid during treatment of certain samples. After each treatment, a small portion of the aqueous phase was shaken for 2 min with solutions of the nickel and vanadyl porphyrins in carbon tetrachloride as a simple check of the effectiveness of the operation. The general procedure adopted for the stocks listed in Table I (p. 5) will be given in detail for a representative case.

South Louisiana gas oil (300 g) was dissolved in benzene and the solution was diluted to 1.2 liters. One-fifth of this solution was shaken for 2 min with 800 ml of hypochlorous acid solution (prepared as above) and 3 liters of water. The aqueous layer decolorized a solution of the nickel complex in carbon tetrachloride in 10 sec and the vanadyl complex in 2.5 min. A 25-ml aliquot, after treatment with potassium iodide and acetic acid, released iodine equivalent to 2.6 ml of 0.1 N sodium thiosulfate. The aqueous phase was filtered through a cotton plug; the filtrate was combined with those obtained from processing the remainder of the benzene solution of the oil, and boiled down to about 100 ml. The solution was clarified with Celite and evaporated to dryness. The residue was evaporated twice with 50-ml portions of 5 N hydrochloric acid and finally heated for 2 hr at 120°. The solid was dissolved in 60 ml of water, and after clarifying again with Celite, the solution was diluted to 100 ml in a volumetric flask. Treatment of a 10-ml aliquot with dimethylglyoxime in ammonia showed that 0.55 mg of nickel was present in the total aqueous-extract from the oil. A check was made on the nickel content of the reagents by evaporating a mixture of water (7.2 liters) and hypochlorous acid solution (1.6 liters) to dryness in a manner similar to that used with the washings from the oil. The correction for extraneous material was 0.028 mg. The nickel removed from the oil was therefore 0.52 mg, or 75.4% of the nickel originally present in the oil.

For the treatment of so-called secondary condensate, 200 g in 400 ml of benzene was treated in four equal portions with 1 liter of hypochlorous acid solution and 3 liters of water. The reliability of the method used for estimation of vanadium was checked by shaking the oil (50 g) and benzene (50 ml) with hypochlorous acid solution (1 liter) and water (3 liters) to which 100 γ of vanadium (equivalent to 2 ppm in the oil) had been added. The vanadium could be detected in the aqueous solution after concentration in the usual manner.

The remaining four oil samples listed in Table I (p. 5) were processed by dissolving 200 g of oil in 400 ml of benzene and treating under the conditions used for secondary condensate. Bachaquero crude, which caused a larger reduction in hypochlorous acid concentration than the other samples, was treated in 33-g batches with 1 liter of hypochlorous acid solution and 4 liters of water.

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