NITROGEN IN OIL SHALE AND SHALE OIL.

VIII. The Detection of Tar Bases.

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Introduction.

In connection with other aspects of this work it became necessary to develop an unambiguous test for the detection of tar bases in crude shale oil and its products.

The tar bases present in shale oil are principally pyridine homologues, though weakly basic pyrrole homologues are also present (Mapstone, 1948). Crude shale oil also contains a large proportion of non-basic nitrogenous compounds of unknown composition (Mapstone, 1949), but these were not of importance in the work described here. Tests carried out on the oil could indicate the presence of either pyridine homologues or of pyrroles, while tests on an acid extract of the oil would be mainly indicative of the pyridine bases because of the very low acid solubility of the pyrroles.

With strongly coloured samples, it was necessary to extract the bases with acid before applying the tests. A number of different tests were therefore examined for sensitivity for the detection of tar bases in solution in the lighter oils and in solution in dilute sulphuric acid as they were extracted from the darker coloured oils.

Samples Tested.

The tar bases present in the acid sludge from the treatment of cracked shale gasoline were considered to be sufficiently representative of those initially present in the gasoline to be used for this work. They were therefore isolated as described previously (Mapstone, 1947) and purified by distillation. They contained 8·69% of nitrogen by weight, and the bases present would be almost entirely pyridine homologues.

Since preliminary work indicated the probable presence of approximately 5 p.p.m. of tar bases in refined shale gasoline, another suitable tar base-free hydrocarbon solvent was required for the determination of the sensitivity of the various reagents. The highly purified *n*-heptane-isoctane blend used for the determination of the octane rating of motor fuels was found to give a negative test with all except a few of the reagents used. In the cases where a positive result was obtained the reaction could be attributed to other factors. A 1% solution of the bases in the heptane-octane mixture (hereafter referred to as gasoline) was carefully prepared and the more dilute solutions prepared from it by dilution with further gasoline.

A solution of the purified bases in dilute sulphuric acid was prepared by dissolving 1·0 ml. of the bases in 250 ml. of 0·097 N sulphuric acid. Titration of portion of the solution showed that the excess acid was 0·0637 N, giving an 0·0333 N solution of the bases. This solution was diluted with further portions of the 0·0970 N acid to give the more dilute solutions required.

The light recycle oil (boiling range 5% at 360° F., 95% at 520° F) from the thermal cracking of crude shale oil is dark brown in colour, and it was therefore

necessary to extract the bases for detection. From the method of extraction and the boiling range the bases would be principally pyridine homologues together with any quinoline homologues that may be present. Fifty millilitres of the oil were washed with 200 ml. of 0·1061 N sulphuric acid. Titration of portion of the solution thus obtained showed that the excess acid was 0·0362 N, giving an 0·0699 N solution of the bases. This was diluted with further portion of the 0·1 N acid to give the more dilute solutions required.

With crude shale oil it was even more necessary than with the light recycle oil to extract the bases before detection. In the manner described for the light oil a 0·042 N solution of the bases from the crude shale oil was obtained in 0·1 N sulphuric acid.

Unless otherwise mentioned the tests on the hydrocarbon samples were carried out by adding two drops of the reagent to 5 ml. of the sample, and the tests on the acid extracts by adding four drops of the reagent to 1 ml. of the sample.

Reagents.

In deciding which reagents were to be tested, those which reacted with pyridine or quinoline or their homologues to give precipitates or developed colours were chosen. Since many alkaloids contain pyridine nuclei several "alkaloid" reagents were included. However, those alkaloid reagents which are based on concentrated sulphuric acid (e.g. Froehde's, Mandelin's and Erdmann's reagents) were not examined because of the action of the acid on the olefines in the gasoline samples, and with the samples dissolved in dilute acid, the dilution of the reagent would render them ineffective.

From the nature of their reaction with the tar bases the reagents were somewhat arbitrarily subdivided into seven classes which are discussed in turn.

(1) *Metal salts which precipitate the metal hydroxide.*

Pyridine and quinoline and their homologues are tertiary amines and their aqueous solutions can be sufficiently alkaline to precipitate the hydroxides from the solutions of the salts of various metals (Perkin, 1935). The sensitivity of the tests with such reagents would therefore depend principally on the solubility of the hydroxide of the metal, and the ease with which it could be seen when precipitated. The reagents were prepared by adding dilute ammonia dropwise to the aqueous solution of the metal salt until a slight permanent precipitate was formed. The reagent solution was used after filtration.

Five per cent. solutions of ferric chloride, cobalt nitrate, nickel nitrate, cupric nitrate and zinc chloride and a saturated solution of potassium alum were prepared in this manner. Another mixed reagent was prepared by the addition of 3 ml. of 1% ammonium aurine tricarboxylate solution to approximately 80 ml. of the saturated alum solution. A slight red precipitate was formed and removed by filtration. It was thought that the dye would be adsorbed on any aluminium hydroxide precipitate and render it more visible and thus possibly increase the sensitivity of the alum reagent.

On carrying out the test on samples with higher tar base concentrations a precipitate was thrown down but, with the limiting concentrations a film was formed at the gasoline-reagent interface. If an excess of reagent was used (e.g. 2 ml. per 5 ml. sample) the cobalt and aluminium reagents gave positive results even in the absence of tar bases. It was therefore necessary to adhere strictly to the test conditions in order to obtain reproducible results. The sensitivities of these reagents are presented in Table 1.

TABLE 1.
Sensitivities of Reagents.
Metal Salts which Precipitate the Metal Hydroxides.

Reagent.	Colour of Precipitate.	Sensitivity.[1]
Ferric chloride	Red to yellow.	0·0001%.
Cobalt nitrate	Pink.	Beyond 0·00005%.
Nickel nitrate	Green.	0·0001%.
Cupric nitrate	Green-blue.	Beyond 0·00005%.
Zinc chloride	White.	Beyond 0·00005%.
Potassium alum	White.	0·001%.
Alum plus ammonium aurine tricarboxylate	Reddish.	0·001%.

[1] Sensitivity is quoted as the least percentage of tar bases (8·7% N) by volume which gave a positive test.

Because the reaction between these reagents and the tar bases involves the precipitation of the acid soluble hydroxides of the metals, they were applicable to the detection of only the free bases and could not be applied to the acid extracts.

(2) *Acids which precipitate insoluble salts of the bases.*

This group of reagents includes many which have been used for the separation, isolation and identification of tar bases, and several " alkaloid " reagents. Because of their varied nature they are discussed separately. The sensitivities of the reagents are presented in Table 2.

TABLE 2.
Sensitivities of Reagents.
Acids which Precipitate Insoluble Salts of the Bases.

Source of Bases.	Gasoline.		Light Oil.	Crude Oil.
Base dissolved in acid ..	Gasoline	0·1 N H_2SO_4.	0·1 N H_2SO_4.	0·1 N H_2SO_4.
Chlorplatinic	0·1%	Nil	Nil	0·0001 N
Chlorauric	0·05%	Nil	0·00007 N	0·00003 N
HCl in ether	0·00005%	—	—	—
HCl (concentrated)	0·005%	—	—	—
Picric	0·001%	Nil	0·02 N	0·0012 N
Styphnic	0·1%	Nil	0·015 N	0·0002 N
Trinitro-*m*-cresol	0·05%	Nil	0·015 N	0·0002 N
Oxalic	0·01%	—	—	—
Tannic	0·2%	Nil	0·03 N	0·003 N
Phosphomolybdic	0·0005%	Nil	Nil	0·0002 N
Phosphotungstic	0·05%	0·003 N	0·00007 N	0·0002 N
Silicotungstic	0·005% p.p.pt. 0·00005% colour	Nil	Nil	0·002 N

The sensitivities are quoted as percentage of tar bases (8·7% N) by volume in the gasoline solution, and as normalitied in the dilute sulphuric acid solutions.

(*a*) *Chlorplatinic Acid.* This reagent precipitates the sparingly soluble platinichlorides of the bases and has been used extensively for this purpose. It is of interest that the earliest recorded isolation and separation of the tar

bases from shale oil involved the precipitation of the bases as their platinichlorides which were separated by fractional crystallization (Williams, 1854, 1855). The reagent was prepared by dissolving 0·0942 gm. of platinum in aqua regia, evaporating the solution to dryness on a water bath, dissolving in 2 ml. of hydrochloric acid and making up to 20 ml. with distilled water. A positive test was indicated by the formation of a yellow-brown precipitate.

(*b*) *Chlorauric Acid.* This reagent is sometimes used to give sparingly soluble amine salts for the separation or identification of tar bases. It was prepared by dissolving 0·1998 gm. of pure gold in aqua regia, evaporating the solution to dryness on a water bath, dissolving in 2 ml. hydrochloric acid and making up to 20 ml. with distilled water. A positive test was indicated by the formation of a yellow-brown precipitate.

(*c*) *Hydrogen Chloride in Ether.* Since the hydrochlorides of the tar bases are insoluble in hydrocarbon solvents, the addition of hydrochloric acid should precipitate the chlorides, and as the precipitate would be soluble in water the sensitivity of the test should be increased by the use of an etherial solution of hydrogen chloride. The reagent was prepared by saturating redistilled ether with hydrogen chloride gas. A positive test was indicated by a yellowish or white cloudiness in the sample. An excess of reagent gave a positive test in the absence of tar bases. This test was suitable for hydrocarbon samples only.

(*d*) *Hydrochloric Acid* (*Concentrated*). This test was based on the considerations outlined in (*c*) above, but since it was an aqueous reagent it was not expected to be quite as sensitive. However, the reagent is always readily available and was therefore included for comparison. A positive result was indicated by a white cloudiness in the sample.

(*e*) *Picric Acid.* This reagent is frequently used for the isolation, separation and identification of basic organic compounds. The reagent was used in the form of the saturated aqueous solution. A positive result was indicated by the formation of a yellow precipitate or a yellow film at the gasoline-reagent interface.

(*f*) *Styphnic Acid.* This reagent is frequently used instead of picric acid for the same purposes and gives similar results which are no doubt due to the similarity of structure (styphnic acid is 3-hydroxy picric acid). The test was carried out as with picric acid and gave similar results.

(*g*) *Trinitro* m-*cresol.* This reagent (3-methyl picric acid) was included for comparison. The test was carried out as with picric acid and gave similar results.

(*h*) *Oxalic Acid.* The oxalates of pyridine homologues have sometimes been used for their separation and identification. The reagent was used as a saturated aqueous solution. A positive result was indicated by a white precipitate or film.

(*i*) *Tannic Acid.* This reagent is commonly employed as an " alkaloid " reagent, and was therefore included in this series of tests. This reagent was used as a 10% aqueous solution. The formation of a brown precipitate indicated a positive result.

(*j*) *Phosphomolybdic Acid.* This " alkaloid " reagent was prepared by the method of Hawke and Bergeim (1937). A positive result was indicated by the formation of a precipitate which was brown in higher concentrations and white in the lower concentrations. An excess of reagent gave a white precipitate even in the absences of the bases.

(*k*) *Phosphotungstic Acid.* This " alkaloid " reagent was prepared by the method of Hawke and Bergeim (1937). The test was carried out by adding two drops of the reagent to 5 ml. of the sample. A positive result was indicated by

the formation of a precipitate the colour of which increased from orange-yellow to white with decreasing tar base concentration.

(*l*) *Silicotungstic Acid.* This " alkaloid " reagent was prepared by dissolving 2 gm. of sodium tungstate in 10 ml. of hot water, adding 5 ml. of syrupy sodium silicate solution (s.g. 1·7), acidifying with 2 N nitric acid, diluting with 100 ml. of water, boiling and filtering. The clear filtrate was then acidified with 5 ml. of concentrated nitric acid. The tests were carried out using twice the usual proportion of the reagent. A positive test was indicated by the formation of a light brown precipitate or, in greater dilution, a pink colour in the gasoline sample.

(3) *Alkali salts which precipitate a salt of the base.*

(*a*) *Potassium Ferrocyanide.* This reagent is used for the detection of pyridine (Perkin, 1935) because of the low solubility of pyridine ferrocyanide. The reagent was used in the form of a saturated aqueous solution. A positive result was indicated by the formation of a white precipitate with the lower boiling bases to deep brown precipitate with the higher boiling bases.

(*b*) *Potassium Dichromate.* This reagent is commonly used for the detection of quinoline (Perkin, 1935) because of the sparing solubility of quinoline dichromate. The reagent was used in the form of a saturated aqueous solution A positive result was indicated by the formation of a yellow-orange to dark brown precipitate, the colour increasing with boiling point of the bases.

(*c*) *Potassium Triiodide.* This " alkaloid " reagent was prepared by dissolving 2 gm. of iodine and 4 gm. of potassium iodide in 100 ml. of water. A positive result was indicated by the formation of a brown precipitate.

The results of these tests are presented in Table 3.

TABLE 3.

Sensitivities of Reagents.

(*a*) Salts which precipitate a salt of the Base.
(*b*) Reagents which precipitate a double salt of the Base.
(*c*) Miscellaneous.

Source of Bases.	Gasoline.		Light Oil.	Crude Oil.
Bases dissolved in	Gasoline.	0·1 N H_2SO_4.	0·1 N H_2SO_4.	0·1 N H_2SO_4.
Reagent :				
Potassium ferrocyanide ..	0·5%	Nil	0·03 N	0·005 N
Potassium dichromate ..	0·01%	Nil	0·03 N	0·004 N
Potassium triiodide ..	0·05%	0·001 N	0·00001 N	0·0001 N
Mercuric chloride ..	0·05%	Nil	0·03 N	0·0002 N
Mayer's reagent	0·0005%	0·003 N	0·0007 N	0·0008 N
Dragendorf's reagent ..	0·00005%	0·0002 N	0·00001 N	0·0002 N
Sodium hydroxide ..	—	0·015 N	0·0035 N	0·0002 N
Nessler's reagent ..	0·001%	0·003 N	0·00002 N	0·000002 N

The sensitivities are quoted as percentage of tar bases (8·7% N) by volume in the gasoline solution, and as normalities in the dilute sulphuric acid solutions.

(4) *Reagents which give an insoluble double salt of the bases.*

The reagents discussed in this section could be classified in the previous section as the distinction is one of degree rather than type. The results are therefore presented with them in Table 3.

(*a*) *Mercuric Chloride.* With this reagent pyridine and quinoline and their homologues form complex mercurichlorides, usually of the form $(BHCl)_2HgCl_2$

but frequently the precipitated compound is more complex, e.g. 2·5 dimethyl pyridine gives the compound $C_7H_9N.HCl.6HgCl_2$ (Garrett and Smythe, 1902). The reagent was used in the form of a saturated aqueous solution. The formation of a precipitate indicated a positive result. With the lower boiling bases the precipitate was white, but it was more orange-brown with the crude oil bases.

(*b*) *Potassium Mercuric Iodide* (*Mayer's Reagent*). This " alkaloid " reagent was prepared by dissolving 2·7 gm. of mercuric chloride and 10·0 gm. of potassium iodide in 190 ml. of water. A positive test was indicated by the formation of a precipitate, the colour of which was usually brown but, when near the limiting concentration of bases, was sometimes light brown, cream or even white.

(*c*) *Potassium Bismuth Iodide* (*Dragendorff's or Thresh's Reagent*). This " alkaloid " reagent was prepared by the method outlined by Perkin (1935). A positive test was indicated by the formation of a red-orange precipitate, though the colour sometimes varied to red or brown.

(5) *Reagents which open the pyridine ring.*

The reagents discussed in this section cause the opening of the pyridine ring to give glutaconic aldehyde which forms brightly coloured Schiff's bases with primary aromatic amines.

(*a*) *Thionyl Chloride.* Pyridine can be converted into 4-pyridyl pyridinium chloride on heating with thionyl chloride and on treatment with alkali, this gives glutaconic aldehyde and 4-aminopyridine. Feigl and Anger (1939) developed a test which they reported to be sensitive to five γ of pyridine with a concentration limit of 1 : 10,000 by condensing the glutaconic aldehyde with α-naphthylamine. All attempts to apply this test even to the pure shale tar bases or to pure pyridine yielded negative results.

(*b*) *Cyanogen Halides.* Cyanogen halides react with pyridine to give the unstable *N*-cyano-pyridinium halide which is readily hydrolysed to glutaconic aldehyde. This reaction has been applied to the colorimetric determination of traces of cyanides (Epstein, 1947) as well as pyridine (Barta, 1935) and the detection of alkaloids containing a pyridine ring (Shmuk, 1940, 1942). In this work the three cyanogen halides were tested and the product reacted with a saturated aqueous solution of aniline or a 1% alcoholic solution of *p*-nitro-aniline, anthranilic acid, or α- or β-naphthylamine. The mixture was acidified and the colour change noted. The cyanogen chloride solution was prepared by adding 5 ml. of a 1% chloramine T solution to 2 ml. of a 1 N potassium cyanide solution, The cyanogen bromide and iodide solutions were prepared by adding bromine water or the potassium triiodide solution respectively to a 1 N potassium cyanide solution until there was a slight excess of the free halogen ; this was removed by the addition of a few drops of the cyanide solution. The test was carried out by shaking 5 ml. of the sample with 1 ml. of the cyanogen halide solution followed by the addition of 1 ml. of the amine solution. After the colour had been noted concentrated hydrochloric acid was added dropwise until no further change occurred. With the cyanogen chloride and bromide the tests were satisfactory, but iodine was precipitated on acidification of the tests with cyanogen iodide. The results are presented in Table 4.

(6) *Salts which give co-ordination compounds with pyridine.*

Pyridine is noted for the large number of co-ordination complexes which it forms with metallic salts, but in order that such compounds may be used for the detection of pyridine or its homologues, they should either be insoluble in or extractable from the reaction medium, and should be preferably strongly

TABLE 4.
Sensitivities of Reagents.
Cyanogen Halides and Aromatic Amines.

Source of Bases.	Gasoline.		Light Oil.	Crude Oil.
Bases dissolved in	Gasoline	0·1 N H_2SO_4	0·1 N H_2SO_4	0·1 N H_2SO_4
A. Cyanogen chloride with—				
Aniline :				
Test	y. to r.br.	wh. to c.	wh. to c.	y. to c.
Sensitivity	0·75%	0·003 N	0·000001 N	0·000004 N
p-Nitro-aniline :				
Test	y. to or.	y. to c.	y. to c.	y. to c.
Sensitivity	0·75%	0·015 N	0·000003 N	0·00001 N
Anthranilic acid :				
Test	y. to r.br.	wh. to c.	wh. to c.	y. to c.
Sensitivity	0·75%	0·002 N	0·000001 N	0·000002 N
α-Naphthylamine :				
Test	lt.y. to r.br.	p. to c.	y. to c.	y. to c.
Sensitivity	0·75%	0·003 N	0·000001 N	0·000002 N
β-Naphthylamine :				
Test	y.br. to br.	m. to c.	w. to y.	br. to lt.br.
Sensitivity	0·00005%	0·016 N	0·006 N	0·00002 N
B. Cyanogen bromide with—				
Aniline :				
Test..	y. to r.br.	Nil	cr. to c.	cr. to c.
Sensitivity	0·75%	—	0·00003 N	0·00004 N
p-Nitro-aniline :				
Test	y. to r.br.	y. to c.	y. to c.	cr. to c.
Sensitivity	0·25%	0·003 N	0·00003 N	0·00002 N
Anthranilic acid :				
Test	y. to r.br.	y. to r.br.	y. to c.	cr. to c.
Sensitivity	0·75%	0·016 N	0·000015 N	0·00003 N
α-Naphthylamine :				
Test	br. to r.br.	cr. to c.	cr. to c.	cr. to c.
Sensitivity	0·75%	0·0013 N	0·00003 N	0·00004 N
β-Naphthylamine :				
Test	br. to lt.br.	y.br. to br.	y. to lt.y.	br. to lt.br.
Sensitivity	0·00005%	0·016 N	0·0003 N	0·00004 N

The sensitivities are quoted as percentages of tar bases (10% N) in the gasoline sample, and as normalities in the diluted acid solutions.

Key :

br. = brown. m. = milky. y. = yellow.
c. = colourless. p. = pink. or. = orange.
cl. = clear. r. = red. lt. = light.
cr. = creamy. wh. = white.

coloured. A preliminary survey suggested that the acetates, thiocyanates and cyanates of cobalt, nickel and copper were worth investigation as they were coloured and could be extracted from the aqueous solution by chloroform (Morton, 1946). The results are presented in Table 5.

(*a-c*) *Acetates.* Since the acetates of cobalt, nickel and copper are soluble in water, and the complexes are soluble in chloroform as well as water, they could be extracted satisfactorily from the acid solutions of the bases once formed. A preliminary examination indicated that the complex was stable and could be extracted from the aqueous solution only if the pH was greater than 4. The acetate reagent was therefore prepared to act as a buffer solution as well as to provide acetate ions by dissolving 15 gm. of sodium acetate crystals and 20 ml. of glacial acetic acid in sufficient water to give 100 ml. of solution. The test was

TABLE 5.
Sensitivities of Reagents.
Co-ordination Complexes with Salts.

Source of Bases.	Gasoline.		Light Oil.	Crude Oil.
Bases dissolved in	Gasoline	0·1 N H_2SO_4	0·1 N H_2SO_4	0·1 N H_2SO_4
Salt :				
Cupric acetate	—	0·00025 N	0·00007 N	0·00025 N
Cobalt acetate	—	0·00025 N	0·00015 N	0·00005 N
Nickel acetate	—	0·0005 N	0·0003 N	0·00025 N
Cupric thiocyanate ..	1·0%	0·003 N	0·002 N	0·002 N
Cobalt thiocyanate ..	0·1%	0·007 N	0·0008 N	0·004 N
Nickel thiocyanate ..	0·1%	0·003 N	0·0009 N	0·004 N
Cupric carbamate (?) ..	—	0·001 N	0·002 N	0·0003 N
Cobalt carbamate (?) ..	—	0·0005 N	0·0001 N	0·0001 N
Nickel carbamate (?) ..	—	0·001 N	0·003 N	0·0005 N

The sensitivities are quoted as percentage of tar bases (8·7% N) by volume in the gasoline solution, and as normalities in the dilute sulphuric acid solutions.

carried out by adding 1 ml. of this acetate reagent and 0·5 ml. of a 5% solution of the cobalt, nickel or cupric nitrate, and 1 ml. of chloroform, to 5 ml. of the solution of the tar bases in dilute sulphuric acid. The mixture was shaken and allowed to stand when the development of an amber colour in the chloroform layer indicated a positive test.

With pyridine the cupric acetate complex was green, but with the shale tar bases it was amber. This was first thought to be due to some impurity in the reagent but was later found to be due to the difference in the bases themselves. For comparison the tests were carried out using some pyridine which had been carefully freed from all homologues by refluxing with permanganate, and different boiling fraction of mixtures of pyridine homologues. The lower boiling homologues were obtained by fractionating denaturant grade pyridine (from coal tar) through a 12 pear column and the higher boiling fractions were obtained in previous work (Mapstone, 1947) by the careful fractionation of the shale tar bases through a 36-inch Fenske column at high reflux.

The results obtained are presented in Table 6, and indicate that the boiling range of the bases influence the colour of the complex formed. The tests were carried out on solutions containing two drops of the bases in 5 ml. of 0·1 N sulphuric acid.

Although pyridine gives complexes with salts of substituted acetic acids and its homologues (Morton, 1946 ; Reitzenstein, 1902, 1940), they were not included as it was felt that they would have little advantage, if any, over the acetates.

(*d*) *Cupric Thiocyanate.* The formation of a precipitate, $Cu(CNS)_2.2C_5H_5N$, which is soluble in chloroform to give an emerald green solution, is reported to be sensitive to 0·05% of pyridine (Morton, 1946 ; Spacu, 1922, 1923). In this work the test was carried out by adding two drops of a solution of 5 gm. of potassium thiocyanate in 10 ml. of water and two drops of a 0·5% solution of cupric nitrate to 5 ml. of the sample. This gave a black to greenish black precipitate of cupric thiocyanate. With the acid solutions the complex was extracted by the addition of 2 ml. of chloroform. A positive result was indicated by a green colour in the chloroform. With the acid samples containing the tar bases from gasoline the chloroform coagulated the dark green cupric thiocyanate precipitate and gave a yellowish-white precipitate at the interface. With the gasoline solution of the bases the black precipitate of cupric thiocyanate interfered with the observation of any colour. In this case the precipitate was

TABLE 6.

Effect of Boiling Point of Bases on Colour of Acetate Complex.

Base.	Colour of Complex in Chloroform.		
	Cobalt.	Nickel.	Cupric.
Pure pyridine	Amber.	Yellow-green.	Green.
Coal tar bases to 117° C. ..	Light yellow.	Light yellow.	Green-lemon.
,, ,, 117–133° C. ..	,,	,,	Light green.
,, ,, 133–145° C. ..	,,	,,	Light yellow.
,, ,, 145–155° C. ..	,,	,,	Lemon-green.
Shale tar bases 164–170° C. ..	Very pale bluish green.	Very pale bluish green.	Very pale bluish green.
,, ,, 170–180° C. ..	Yellowish green.	Yellowish green.	Yellowish green.
,, ,, 180–190° C. ..	Yellowish green.	Yellowish green.	Yellowish green.
,, ,, 190–200° C. ..	Yellow.	Yellow.	Yellow.
,, ,, 200–210° C. ..	Yellow.	Yellow.	Yellow.
,, ,, 210–212° C. ..	Greenish amber.	Greenish amber.	Amber.
,, ,, *ex* gasoline ..	Amber.	Amber.	Amber.
,, ,, *ex* light oil ..	Amber.	Light amber.	Amber.
,, ,, *ex* crude oil	Amber.	Light amber.	Amber.

Remarks : The colour developed with the shale tar bases increased in intensity with increasing boiling point. The colours observed ranged through all the various shades mentioned but did not show quite as much difference as may appear to be indicated by the table.

filtered off and washed with 2-3 ml. of chloroform, the washings being collected separately. A positive test was indicated by the formation of a green colour in the chloroform washings.

(*e*) *Nickel Thiocyanate.* These tests were carried out as with the cupric salt using a 5% solution of nickel nitrate. With the solution of tar bases in gasoline a positive test was indicated by the formation of a green colour in the reagent and a white to green interfacial precipitate. Since the nickel thiocyanate was soluble in water the filtration step was not necessary. No precipitate was formed with the acid solutions of tar bases, but a positive test was indicated by the formation of an amber colour in the lower phase on shaking with chloroform.

(*f*) *Cobalt Thiocyanate.* These tests were carried out as with the cupric and nickel salts using a 5% solution of cobalt nitrate. As with the nickel salt, the cobalt thiocyanate did not precipitate and interfere with the observations of the test. With the tar bases in gasoline a positive result was indicated by the formation of a green precipitate. With the acid solutions a positive test was indicated by the formation of a greenish blue colour in the chloroform layer.

(*g-i*) *Cyanates* (*Carbamates*). The formation of the dipyridine complex of cupric cyanate has been described for the detection of copper or cyanate, the complex being soluble in chloroform to give an azure blue solution (Morton, 1946 ; Werner, 1925 ; Vogel, 1945). The complex cobalt and nickel pyridine cyanates are also soluble in chloroform (Morton, 1946 ; Davis and Logan, 1928, 1934). Since potassium cyanate is not readily available commercially, it was prepared by two different methods for comparison ; the oxidation of fused potassium cyanide with litharge, and oxidation in solution with the calculated amount of potassium permanganate. In each case the freshly prepared solution gave the same results, and in each case also the solution decomposed on standing, so that no cyanate could be detected in the reagent solution after standing for a few hours even though the test applied was sensitive to one part of cyanate in 20,000 (Vogel, 1945), although this solution still gave

colour reactions with the tar bases, of comparable sensitivity with the acetates and thiocyanates. Hydrolysis of the cyanate would give a carbamate and then a carbonate, but carbonates did not give the colour reactions. It is therefore suggested that the colour reactions observed are due to the formation of complex pyridine cupric carbamate and the corresponding cobalt and nickel salts.

The cyanate (or carbamate) reagent was prepared by adding a solution of 5·5 gm. (0·033 gm. mol) of potassium permanganate in 40 ml. of water containing 3·3 ml. (0·033 mol) of concentrated hydrochloric acid to a solution of 3·3 gm. (0·05 mol) of potassium cyanide, followed by suction filtration to remove the precipitated manganese dioxide. The object of adding the acid was to neutralize the potassium hydroxide formed during the oxidation, but it did not appear to stabilize the cyanate solution and could be omitted without effect. The test was applied to the acid solutions of the bases only, as significant results could not be obtained with the gasoline solution of the bases. The test was carried out by adding two drops of the cyanate solution and two drops of the metal nitrate solution (as for the thiocyanate tests) to 5 ml. of the sample. Dilute (5%) acetic acid was added dropwise until the precipitated (hydroxide and/or carbonate of the metal) dissolved and the complex then extracted by shaking with 2 ml. of chloroform. A positive result was indicated by the formation of a colour in the chloroform layer. With a cyanate solution that had been freshly prepared the colours obtained were: copper, light blue; cobalt, royal blue; nickel, pale green. If the cyanate solution had been prepared for more than half an hour the colours obtained were: copper, green to amber, depending on the boiling range of the bases; cobalt, amber to red; nickel, orange to brown. Because of the instability of the fresh reagent the sensitivity of the test with only the more stable hydrolysed solution was determined.

(7) *Miscellaneous tests.*

In this section are listed those tests that cannot be included in any of the previous categories. The results are presented in Table 3.

(*a*) *Sodium Hydroxide.* Addition of this reagent to an acid solution of the bases liberates the free bases. Although pyridine itself is completely miscible with water, the solubility of the homologues decreases rapidly with increasing molecular weight. The test therefore depends on the sparing solubility of the liberated mixture of the bases in water. The reagent was used as a 10% aqueous solution and a positive result was indicated by the formation of a white precipitate or white cloudiness.

(*b*) *Condensation with Sodium 1 : 2-naphthaquinone-4-sulphonate.* Feigl and Frehden (1934) observed that *N*-alkyl pyridinium compounds readily condense with 1 : 2-naphthaquinone-4-sulphonic acid to give coloured compounds. The test was carried out using methyl iodide and dimethyl sulphate as alternative alkylating agents and gave yellow to red colours with the bases. However, similar colours were obtained in the absence of the bases when the test was applied to the gasoline and sulphuric acid used to dissolve the bases. This may be due to the condensation of the sulphuric acid reagent with other reactive compounds (Erlich and Herter, 1904).

(*c*) *Nessler's Reagent.* This reagent is the most sensitive reagent known for the detection of ammonia and has recently been shown to be even more sensitive for the detection of aromatic secondary amines than for ammonia (Liebhafsky and Bronk, 1948). Nichols and Willits (1934) thoroughly investigated the reaction of the reagent with ammonia and concluded that the product was a colloidal suspension of the composition $NH_2Hg_2I_3$. Primary and secondary amines could therefore be expected to give the analogous products $RNH.Hg_2I_3$

and $NR_2Hg_2I_3$ respectively, and the tertiary amines may be expected to react as with Mayer's reagent. This reagent was prepared in the manner described by Perkin (1935). When tested with the heptane-octane mixture the reagent gave a slight yellow-green precipitate on standing for 10-15 seconds, in the absence of added tar bases. Because of this the sensitivity of the reagent for the detection of tar bases in gasoline solution was determined with solutions of the bases in a sample of the gasoline that had been washed with the reagent until no further precipitate was formed, and then water washed and filtered. The formation of a precipitate in the absence of added tar bases was probably due to the presence of aldehydes in the gasoline as it has been shown that Nessler's reagent can give a positive response to 1 p.p.m. of acetaldehyde in ether (van Deripe, Billheimer and Nitardy, 1936). With the solution of the bases in gasoline a positive test was indicated by the formation of a precipitate, the colour of which was usually greenish-yellow but, when near the limiting concentrations, was yellow to cream. With the acid solutions of the bases the reagent gave a white to cream precipitate.

Summary.

Fixty-four different tests have been examined for their sensitivity for the detection of shale tar bases (essentially pyridine homologues). Thirty-nine of the tests are suitable for the detection of the lower boiling bases in solution in gasoline ; 26 for the detection of the bases from the gasoline in solution in dilute acid ; 33 for the detection of the bases from the light oil in solution in dilute acid ; and 36 for the detection of the bases from the crude oil in solution in dilute acid.

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