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PROCESS OF RECOVERING NITROGEN BASES

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This invention relates to the recovery of nitrogenous compounds from hydrocarbon matter, and has for a principal object the separation of the so-called nitrogen bases from petroleum or any of its fractions.

It is an object of the invention to provide a highly efficient recoverable reagent so that the nitrogen bases may be extracted with a minimum consumption of chemicals.

Another object of the invention is the recovery of larger amounts of nitrogen bases than are obtainable by methods heretofore known.

Yet another object of the invention is the separation of different types of nitrogen bases from one another.

Other more specific objects will be apparent in the following description of the invention.

It is well known that there is present in petroleum and distillates thereof a small percentage of organic nitrogen compounds, particularly in oils of naphthenic origin such as those obtained from California fields. Some of these nitrogen compounds show basic character in that they are reactive with dilute acids and consequently they are known as "nitrogen bases".

Methods for the separation of nitrogen bases from petroleum have been known for some time. For example, Ihrig (U. S. Patents Nos. 1,686,136 and 1,768,910) extracts the hydrocarbon oil containing nitrogen bases with 25% sulphuric acid and then neutralizes the extract with caustic soda, whereupon the nitrogen bases are thrown out as an immiscible layer. More recently, Bailey prefers (U. S. Patent No. 2,035,583) to wash partially degassed sulphur dioxide extracts with water whereby the residual sulphur dioxide dissolves in the water to form sulphurous acid. A portion of the nitrogen bases combines with the sulphurous acid to form some sort of compounds which, in order to fix our ideas, we may call nitrogen base acid sulphites. The aqueous solution of the nitrogen base acid sulphites is then neutralized with a caustic solution whereupon the nitrogen bases are released.

Mahan and Bailey (J. A. C. S. 59, 449—1937) have described a method for the purification of nitrogen bases in which a salt of the composition $(Base)_2 \cdot ZnCl_2$ is first prepared by contacting the crude bases with zinc chloride solution at 80° C., for about one hour. The water and/or other impurities are then distilled off and when this step has been completed the still contains the anhydrous double salt $(Base)_2 \cdot ZnCl_2$. A dried condenser and receiver are connected to the still and the heating continued to a temperature somewhat beyond the dissociation temperature (320° C. or higher) of the double salt. The nitrogen base then distills off and is recovered in the receiver. In this way Mahan and Bailey were able to obtain nitrogen bases free of sulphur compounds and other common impurities.

While the above method is very useful as a laboratory procedure, the use of solid cakes presents obvious industrial difficulties. All of the industrial methods listed above use caustic soda as a neutralizing agent. The use of this chemical is undesirable because it is rarely economically recoverable and, besides the consumption of caustic soda itself, the disposal of the soda salts formed in the neutralization reaction is often burdensome. A process which will eliminate losses of chemicals is therefore a desirable one from this point of view alone.

In addition to the above mentioned drawbacks of conventional processing the use of dilute sulphuric acid or other mineral acids is undesirable because of their severe corrosiveness to equipment. Dilute mineral acids are corrosive even to lead. Obviously, concentrated sulphuric acid of a strength in excess of about 70% cannot be considered because of the formation of sludge which accompanies the use of this reagent in treating petroleum oils. Such sludges would severely contaminate the product sought. Aqueous solutions of sulphurous acid are also corrosive to equipment, but to a lesser extent than aqueous sulphuric acid solutions. As a result of the corrosion of the equipment, particularly when iron is exposed to the reagent, a flocculent precipitate of ferric and ferrous hydroxides is formed after the extract is neutralized. This precipitate firmly occludes a large portion of the nitrogen bases. Pressing the precipitate removes a part of the occluded bases, but a substantially complete recovery of the bases requires the washing of the precipitate with a suitable solvent such as benzene, diethyl ether or acetone.

A less obvious disadvantage of the older methods is that only a small portion of the nitrogen bases is recovered from the oil when dilute mineral acids such as dilute sulphuric and hydrochloric acid are used as extractants. A possible conclusion of this observation is that nitrogen compounds of a wide range of basic strength exist in petroleum oils.

It has been postulated that the basic nitrogen compounds are formed from more complex structures by pyrolysis during distillation. If this is correct, the yield of nitrogen bases from petroleum or its fractions which have been sub-

jected to high temperatures for a relatively prolonged period of time should be greater than from similar material which has been heated for a relatively short time. Further, one may expect that in petroleum products obtained from pyrolytic processes the aromatic nitrogen bases would predominate, because dehydrogenation of the original hydroaromatic bases occurs at high temperatures. These assumptions have been substantiated by experiments which show that the pressure distillate or recycle gas oil fractions from cracking operations show particularly high yields of nitrogen bases, predominantly of the aromatic type when compared to straight run distillates of the same source.

In its essentials, our process comprises treating petroleum or a fraction thereof containing either or both of the above types of nitrogen bases with a volatile organic acid such as a fatty acid of low molecular weight. After separation, the acid layer is subjected to a distillation. Under the influence of heat, the nitrogen base salts dissociate and the relatively volatile organic acid vaporizes whereas the relatively non-volatile nitrogen bases remain liquid. The organic acid is thus taken overhead and recovered separately from the nitrogen bases which remain as a distillation residue. The recovered acids may then be used for treating a new charge of oil.

In this process, the treatment with fatty acid is preferably conducted at atmospheric pressure and temperature, although in the treatment of heavy fractions it will be advantageous to use higher temperatures, and to maintain pressure sufficient to prevent any substantial loss of the volatile fatty acid. Obviously, the purpose of the higher temperature is to obtain a reduction in the viscosity of the material to be treated, and in this way to facilitate an intimate dispersion of the fatty acid droplets in the main body of oil.

Atmospheric temperatures are preferred for two reasons. First, there is the obvious reason of economy. Second, since the fatty acid nitrogen base salts are dissociable, increased temperatures will result in partial dissociation of the salts and a portion of the extractable nitrogen bases will remain in the oil. In this way, yields would tend to be reduced. Therefore, it is advisable in such cases, where the viscous nature of the raw material demands it, to contact the oil with the extraction medium at elevated temperatures under pressure, and then to cool the mixture before separating the layers, to avoid dissociation of the nitrogen base salts. Alternatively, the heavier fractions may be diluted with a light naphtha or kerosene, and a reduction in viscosity may be obtained in this way. This method of operation will eliminate the necessity of using relatively expensive pressure equipment. The diluent itself may or may not contain nitrogen bases. If it does contain them, it would be necessary to fractionate the recovered nitrogen bases in case only heavy nitrogen bases are sought. On the other hand, if the volatility or the molecular weight of the desired product is of no consequence, the fractionation would be unnecessary.

In certain cases, it may even be advantageous to treat at sub-atmospheric temperatures, particularly in summer months, or even throughout the year. It must be remembered that petroleum is a highly complicated mixture containing a large number of components, and the determination of the best conditions in any special case must necessarily remain a question of experimentation.

Besides the fact that the volatile fatty acids are economical treating reagents by virtue of their recoverability, we have found that they extract a considerably larger portion of the nitrogen compounds than 18% sulphuric acid. Of the fatty acids, formic acid was found to be the best suited because of its relatively high volatility and the negligible solutility of hydrocarbons in it. Aqueous formic acid of 90% concentration is available in commercial quantities and is suitable for use in the process, although formic acid of other strengths may be more desirable as hereinafter set forth. Acetic acid is also a desirable treating agent insofar as it is about as volatile as formic acid. However, glacial acetic acid is not entirely satisfactory because it dissolves appreciable amounts of hydrocarbon matter. Aqueous solutions of acetic acid, particularly solutions of less than 90% acetic acid concentration are free from this objection. Similarly, aqueous solutions of other volatile organic acids could be used.

The following experiments and the table of results exemplify the superiority of the present process using formic acid over the older sulphuric acid method. To the economically desirable feature of larger yields must be added the substantially complete elimination of chemical losses and the simplification of the method of operation.

Experiment 1

Twenty-five gallons of a straight run gas oil derived from California (Coalinga) crude oil, were agitated with one gallon of 18% H_2SO_4. The batch was allowed to settle and the lower layer (aqueous sulphuric acid-nitrogen base solution) was withdrawn. A considerable volume of precipitated lead sulphate was filtered, and the filtrated causticized with sodium hydroxide. A flocculent precipitate of ferric and ferrous hydroxides appeared. This was filtered off and thoroughly washed with acetone. A portion of the nitrogen bases which were released upon neutralization appeared in the filtrate. This filtrate was extracted with A. S. T. M. ether. The acetone washings of the precipitate were evaporated on a steam bath and the residue combined with the A. S. T. M. ether extract. The residue after evaporation of the A. S. T. M. ether comprises the recovered nitrogen bases.

Experiment 2

This is the same as Experiment 1 except that the gas oil was pre-washed with a slight excess of caustic soda to remove naphthenic acids. The yield of N-bases was identical with that in Experiment 1.

Experiment 3

Five gallons of straight run California (Coalinga) gas oil were agitated with 4% by volume of 30% formic acid. After settling, the lower layer comprising the formic acid and nitrogen bases was separated and distilled. After the water and formic acid were carried overhead, the heating was stopped. The residue was washed out of the flask with diethyl ether and filtered. The diethyl ether was then evaporated on a steam bath and the nitrogen bases weighed.

Experiment 4

Five gallons of a straight run California (Kern) gas oil were treated with 4% by volume of 30%

formic acid (757 cc.) at atmospheric temperature. After settling, the lower layer, containing the formic acid and the extracted nitrogen bases, was withdrawn and then distilled. When the aqueous formic acid had been driven off, the heating was discontinued. The still bottoms were washed out with diethyl ether, filtered and the diethyl ether evaporated on a steam bath. The residue comprising the extracted nitrogen bases was weighed.

Experiment 5

Five gallons of a straight run California (Kern) spindle oil distillate having a viscosity of about 120 seconds S. U. at 100° F., was treated with 4% by volume of 10% formic acid (757 cc.) at atmospheric temperature. After settling, the lower layer containing the formic acid and extracted nitrogen bases was withdrawn and then distilled. When the aqueous formic acid had been driven off, the heating was discontinued. The still bottoms were washed out with diethyl ether, filtered and the diethyl ether evaporated on a steam bath. The residue comprising the extracted nitrogen bases was weighed.

Experiment 6

The same as Experiment 5 except that the formic acid concentration was 30%.

Experiment 7

The same as Experiment 5 except that the formic acid concentration was 50%.

Experiment 8

The same as Experiment 5 except that the formic acid concentration was 70%.

Experiment 9

The same as Experiment 8 except that straight run (California, Kern) gas oil was used.

Experiment 10

The same as Experiment 9, substituting for the straight run gas oil, a cracked gas oil of the same boiling range, derived from the same crude.

Experiment 11

A continuous countercurrent extraction in a packed glass column 1 inch in diameter and five feet in length, using the same cracked gas oil as Experiment 10, and 70% formic acid at a rate of 12% by volume of the oil. The formic acid portion was distilled and the residue washed out of the still with diethyl ether and weighed after evaporation of the ether.

Experiment 12

A three batch extraction, on another portion of the same cracked gas oil used in Experiments 10 and 11, using 70% formic acid at a rate of 4% by volume in each step. Thus the total formic acid rate is 12% as in Experiment 11. The formic acid extracts were combined and then distilled. The remainder of the procedure was the same as in the preceding experiments.

It must be noted that while diethyl ether was used to wash out the distillation residue in the foregoing experiments, this was done only to obtain greater accuracy in the yield determinations. It is obvious that this should be considered only as a laboratory expedient and not as an essential step in the process. When operating for any purpose which does not require an analytical determination of the yields, the ether wash could be eliminated. Naturally, the use of ether is not contemplated in commercial operation. The results of the experiments are summarized in the following table:

Table

Experiment No.	Acid used	Treatment	Acid concentration	Oil used	Yield N-bases	N in bases	Refractive index N-bases	Specific gravity N-bases	N in oil	
									Before treatment	After treatment
			Percent by weight		*Percent*	*Percent*			*Percent*	*Percent*
1	H_2SO_4	(B)	18	CGO	0.07	5.60	1.5458			
2	H_2SO_4	(B)	18	CGO	0.07	5.63	1.5460			
3	HCOOH	(B)	30	CGO	0.06	5.2	1.5420	0.994		
4	HCOOH	(B)	30	KGO	0.07	4.8	1.5330	0.986		
5	HCOOH	(B)	10	KSO	0.02	(1)	(1)	(1)	(1)	(1)
6	HCOOH	(B)	30	KSO	0.09	5.1	1.5670	1.019		
7	HCOOH	(B)	50	KSO	0.40	4.7	1.5610	1.019		
8	HCOOH	(B)	70	KSO	1.21	4.5	1.5590	1.016		
9	HCOOH	(B)	70	KGO	0.44	4.8	1.5305	0.996	0.037	0.012
10	HCOOH	(B)	70	CRGO	1.01	5.96	1.550	1.019	0.135	0.050
11	HCOOH	(CC)	70	CRGO	1.65	5.05	1.560	1.023	0.135	Trace
12	HCOOH	(3B)	70	CRGO	1.50	5.17	1.558	1.021	0.135	0.012

[1] Insufficient sample.
(B)=batch treatment.
(CC)=counter-current treatment.
(3B)=three-batch treatment.
CGO=Coalinga gas oil.
KGO=Kern gas oil.
KSO=Kern spindle oil.
CRGO=cracked Kern gas oil.

From an inspection of the table several points of interest are apparent. First, the great increase in the yields of nitrogen bases when using 70% formic acid over 18% sulphuric acid is shown in Experiments 1, 2, 3, 4, and 9. It is clear that 30% formic acid and 18% sulphuric acid are about equivalent with respect to the yields (Experiments 1, 2, 3). Further, Kern and Coalinga gas oils give about the same yields with 30% formic acid (Experiments 3, 4). Experiment 9 using 70% formic acid shows a yield of 0.44% compared to a yield of 0.07% in Experiment 4 using 30% formic acid. Since the two last experiments were made on material from the same source, it follows that the increased yield is due to the action of the 70% formic acid. Experiments 5, 6, 7, and 8 confirm this point of view as they show increasing yields with increasing formic acid concentration.

Experiments 11 and 12 are illustrative of the effectiveness of counter current processing versus repeated batch processing. The superiority of the

counter current treatment is quite obvious and is in accord with the well known fact that counter current operation in general is more effective than batch operation using the same rate of extractant.

Whereas it has been claimed that nitrogen bases are completely extracted from petroleum or the fractions thereof by liquid sulphur dioxide, we have found that this is not the case, although there is a rather pronounced selective solubility effect which tends to concentrate the nitrogen bases in the sulphur dioxide extract. According to Experiment 11, however, it is apparent that by our process we have succeeded in separating and recovering substantially all of the nitrogen bases present in the oil, whereas by hitherto known processes, this cannot be done without injury to the oil or the nitrogen bases, or both. Furthermore, it is obvious that our method of extracting nitrogen bases can be applied also to extracts from solvent treating operations, in which the nitrogen bases may be concentrated, as stated before.

It is of interest to note that the bases extracted with formic acid of a concentration of 30% or less are completely soluble in ten times their volume of 50% sulphuric acid. On the other hand, the bases extracted with formic acid of 50% or 70% strength are only partly soluble in sulphuric acid. The insoluble portion, however, cannot be considered to be hydrocarbon matter as it contains only slightly less nitrogen than the total extracted bases.

It appears that the more concentrated formic acid is capable of extracting a different type of nitrogen compounds, as well as the nitrogen bases extractable with dilute sulphuric acid. These nitrogen compounds which are insoluble in dilute sulphuric acid may possibly be considered as not of a basic nature. However, as these compounds are soluble in strong formic acid and, as has been found, in sulphuric acid of a greater concentration than 70%, we prefer to consider them as nitrogen bases, though of a different type than those soluble in dilute sulphuric acid. It should be noted, however, that strong sulphuric acid is not a suitable agent for recovering these compounds due to its tendency to react with the hydrocarbons present and form sludge.

We have found that it is possible to fractionate the extracted bases easily by progressively diluting the formic acid extract with water and separating the released nitrogen bases after each dilution. It may sometimes happen that a separation will not take place readily because of the small difference between the densities of the nitrogen bases and the diluted formic acid. In such cases, the released nitrogen bases can be separated by contacting the suspension with a volatile naphtha. In this way, a clean separation is readily obtained, the naphtha dissolving the released nitrogen bases and simultaneously increasing the difference in density of the two phases.

However, the presence of the volatile naphtha, particularly if it is used in large quantities will change the phase relationship between the released nitrogen bases and the diluted formic acid because it will act as a selective solvent for the nitrogen bases, and the result of the fractionation at a given dilution will not be identical with the naphtha as it would be without it. Nevertheless, by a proper control of the extent of the dilution and the proportion of the naphtha used, it will be possible to obtain any fractionation desired.

It is clear that the same result may be obtained by treating the oil in a series of steps using formic acid of progressively increasing concentration in each step. The formic acid layers from each treatment may then be separately distilled to separately recover the acid and nitrogen bases.

These processes are sometimes undesirable because they may give rise to large volumes of material to be treated. In such cases, it is preferable to carry out the regular process to its completion, thereby obtaining the nitrogen bases free from formic acid; the nitrogen bases may then be extracted several times with formic acid of progressively increasing strength, removing the extract at each step and separately recovering the nitrogen bases as a series of fractions. Alternatively, after the formic acid process has been carried to completion and the nitrogen bases obtained free from formic acid, the thus obtained bases may be fractioned by treatment with a dilute mineral acid, such as sulphuric acid or hydrochloric acid, whereby one type of the nitrogen bases is dissolved. After separation of the insoluble nitrogen bases from the acid phase the type of nitrogen bases soluble in the mineral acid may be recovered by the customary method of neutralization with an alkali.

The extracted bases are ordinarily dark colored oily liquids. They can be much improved in appearance by distillation. The most convenient arrangement for carrying out this distillation for the purpose of purification will be apparent to anyone skilled in the art of distillation, but it may be stated that generally the boiling range of the nitrogen bases is from 50 to 100° F. higher than the boiling range of the hydrocarbon matter from which they are extracted. It is clear that the distillation for the purpose of purifying the nitrogen bases may be combined with the distillation for the recovery of the formic acid, the two operations being carried out simultaneously, for example, with a continuous still and fractionating tower. In such an operation the formic acid vapors could be carried overhead and the various fractions of nitrogen bases obtained as side streams.

The nitrogen bases extracted from the lighter petroleum distillates such as the kerosenes and naphthas are of value as sources of raw materials in the chemical industry as substitutes for the more expensive coal tar derivatives, such as pyridine, quinoline, and their homologues. Both the light and heavy nitrogen bases have found applications as insecticides, and recently it has been found that nitrogen bases from transformer oil are efficient germicides. As previously mentioned, there is a greater variety of types of nitrogen bases in petroleum than in coal tar, which obviously makes the petroleum bases more valuable for synthetic processes.

We claim as our invention:

1. The process of separating nitrogen bases from petroleum oil containing the same which comprises: contacting the oil with a low molecular weight fatty acid of higher volatility than said nitrogen bases, the quantity and concentration of said acid being insufficient to dissolve substantial amounts of hydrocarbon matter, whereby there is formed an oil phase and an acid phase containing nitrogen bases, removing the acid phase, and distilling the same to separately recover the fatty acid and the nitrogen bases.

2. The process according to claim 1 in which the fatty acid is formic acid.

3. The process according to claim 1 in which the fatty acid is acetic acid.

4. The process of separating nitrogen bases from petroleum oil containing the same which comprises: contacting the oil with a low molecular weight fatty acid of higher volatility than said nitrogen bases, the quantity and concentration of said acid being insufficient to dissolve substantial amounts of hydrocarbon matter whereby there is formed an oil phase and an acid phase containing nitrogen bases, removing the acid phase, distilling the same to separately recover the fatty acid and the nitrogen bases, and recycling said recovered fatty acid as a contacting reagent.

5. The process of separating nitrogen bases from petroleum oil containing the same which comprises: contacting the oil with an aqueous solution of a low molecular weight fatty acid of higher volatility than said nitrogen bases, the concentration of said solution of said acid being in the range of from 10% to 90% by weight, and the quantity of said solution being insufficient to dissolve substantial amounts of hydrocarbon matter whereby there is formed an oil phase and an acid phase containing nitrogen bases, removing the acid phase, and distilling the same to separately recover the fatty acid and the nitrogen bases.

6. The process according to claim 5 in which the fatty acid is formic acid.

7. The process according to claim 5 in which the fatty acid is acetic acid.

8. The process of separately recovering nitrogen bases of a plurality of types from petroleum oil containing the same which comprises: contacting the oil with a low molecular weight fatty acid of higher volatility than said nitrogen bases whereby there is formed an oil phase and an acid phase containing nitrogen bases, removing the acid phase and distilling the same to separately recover the fatty acid and the nitrogen bases, then contacting said recovered nitrogen bases with a dilute acid whereby there is formed a nitrogen base phase and an acid phase containing other nitrogen bases, separating said nitrogen base phase and separately recovering said other nitrogen bases from said acid phase.

9. The process according to claim 8 in which the dilute acid is a fatty acid.

10. The process according to claim 8 in which the dilute acid is a mineral acid.

11. The process of separately recovering nitrogen bases of a plurality of types from petroleum oil containing the same which comprises: contacting the oil with a low molecular weight fatty acid of higher volatility than said nitrogen bases whereby there is formed an oil phase and an acid phase containing nitrogen bases, removing the acid phase, distilling the same to separately recover therefrom the fatty acid and nitrogen bases, then contacting the recovered nitrogen bases in a plurality of steps with formic acid of progressively increasing concentration, separating the acid layers from each contacting step and separately distilling each acid layer to separately recover the nitrogen bases and formic acid.

12. The process of separating nitrogen bases into a plurality of types which comprises: contacting a body of nitrogen bases in a plurality of steps with aqueous formic acid of progressively increasing concentration, whereby there is formed in each step a nitrogen base phase and an acid phase containing nitrogen bases, separating each acid phase, and separately distilling each acid phase to separately recover the aqueous formic acid and the nitrogen bases dissolved therein.

13. The process of separating nitrogen bases from petroleum oils containing the same which comprises: reducing the viscosity of the petroleum oil by dilution with a petroleum oil of low viscosity, then contacting with a low molecular weight fatty acid of higher volatility than said nitrogen bases, the quantity and concentration of said acid being insufficient to dissolve substantial amounts of hydrocarbon matter, whereby there is formed an oil phase and an acid phase containing nitrogen bases, removing said acid phase, and distilling the same to separately recover the fatty acid and the nitrogen bases.

14. The process of separating nitrogen bases from petroleum oils containing the same which comprises: contacting the oil in a closed system at elevated temperature with a low molecular weight fatty acid of higher volatility than said nitrogen bases, the quantity and concentration of said acid being insufficient to dissolve substantial amounts of hydrocarbon matter whereby there is formed an oil phase and an acid phase containing nitrogen bases, cooling the system, removing said acid phase, and distilling the same to separately recover the fatty acid and the nitrogen bases.

15. The process of separating nitrogen bases from petroleum oil containing the same which comprises: contacting the oil with a low molecular weight fatty acid of higher volatility than said nitrogen bases whereby there is formed an oil phase and an acid phase containing nitrogen bases, removing said acid phase and distilling the same to separately recover the fatty acid and purified nitrogen bases as distillates.

16. In a process wherein a petroleum oil containing nitrogen bases is treated with a low molecular weight fatty acid of higher volatility than the nitrogen bases thereby forming an oil phase and an acid phase containing impure nitrogen bases, and wherein said acid phase is removed from said oil phase, the steps which comprise: removing the acid from the acid phase by distillation and fractionally distilling the impure nitrogen bases to separate substantially pure nitrogen bases from the impurities.

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