

## UNITED STATES PATENT OFFICE

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## PROCESS OF RECOVERING ORGANIC ACIDS

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The principal object of this invention is the separation of naphthenic and other organic acids from hydrocarbon materials, such as petroleum or any fraction thereof, in such a manner that the reagents used in said separation may economically be recovered and reused in subsequent separations.

Another object is the separation of naphthenic acids, or fatty acids, from petroleum or any of its fractions in such a manner that such separated acids are substantially free from phenolic compounds and other weakly acidic compounds present in the petroleum.

Other objects will become apparent from the following description.

There are a number of more or less well established methods for the recovery of organic acids present in hydrocarbon mixtures such as petroleum distillates and the like. In general, these methods consist in treating the oils with an aqueous solution of a caustic alkali, such as sodium or potassium hydroxide, or with an aqueous solution of sodium carbonate in which the organic acids combine with the alkali to form water soluble soaps which enter the aqueous phase.

Stratification into two layers is then induced either by settling alone, or else, in case emulsions form, by heating or adding emulsion breakers. The aqueous phase is separated and acidified, whereupon the soaps are decomposed and the free acids separate out as a distinct layer which may then be dried. This layer constitutes as such, crude organic acids. These operations may be carried out on crude petroleum, raw distillates of any volatility or viscosity, or distillates that have been subjected to the usual treating processes, either with sulfuric acid or with selective solvents.

Such extraction methods with caustic alkalis or alkali carbonates have several inherent disadvantages, each of which is obviated in the practice of this invention.

First, in order to set free the organic acids from the water soluble soap solution, a sufficient quantity of mineral acid, ordinarily sulfuric acid, is employed to decompose the soap and, in addition, to neutralize the excess alkali present. Neither the alkali used for extracting the soaps, nor the acid used in their decomposition, are economically recoverable, but on the contrary, are converted into useless salt solutions the disposal of which is sometimes burdensome.

Second, the presence of any excess sulfuric acid which may have been added during the decomposition of the soaps causes corrosion of the metals ordinarily used in plant apparatus and results in

either frequent replacement of ordinary apparatus or the use of apparatus constructed of expensive alloys, platings, glass, or the like.

Third, in the use of caustic alkalis, all types of acidic compounds are extracted from the oil along with the desired naphthenic or fatty acids, e.g., phenolic compounds of the type  $\text{R}-\text{OH}$  are extracted together with the desired acids of the type  $\text{R}-\text{COOH}$ , and subsequent processing is necessary to separate these two types of bodies.

Naphthenic acids, and particularly soaps of naphthenic acids, have found extensive use in a number of arts. For example, naphthenic acid soaps are used as detergents in the textile industry, as blending agents for special lubricants, and as catalytic drying ingredients of paints and varnishes. Depending on the use to be made of the naphthenic acids, or of the soaps made therefrom, it is generally desirable, and in some cases essential, that the naphthenic acids be free from certain impurities, especially phenols and other weakly acidic bodies. Freedom from phenols in particular is an essential requirement for acids used in the preparation of naphthenic soaps for the manufacture of paints and specialized lubricants. This is true not only because metal naphthenates which are free from phenolates are more compatible with hydrocarbon materials, but also because the presence of phenolates produces undesirable chemical reactions. For example, in paints, the presence of phenolic bodies tends to resist the normal oxidation and drying of the paint. Also, in lubricants, phenolic bodies exhibit a thermal instability detrimental to the use of the lubricant at elevated temperatures.

Certain processes are known for removing phenols from naphthenic acids but these operate without the economic recovery of the treating agent. This invention overcomes the drawbacks of conventional processes by the use of a novel, economical and efficient process for removing and recovering the naphthenic acids in substantially pure form. The products of this process are substantially free from phenols, and moreover, can be prepared very economically because the treating reagent is recoverable.

In general, application of the invention comprises the treatment of hydrocarbon, or other oily material, containing acidic material to be recovered with ammonia or an amino compound, or other basic compound, by the use of which the soaps formed in the reaction are susceptible to a relatively simple decomposition yielding the component acidic and basic materials. Coupled with this broad principle is the selective removal of

acidic compounds to recover desired acids in pure form.

As illustrative of the above, a crude hydrocarbon oil, or fraction thereof, or other material, containing either desired acids alone or a mixture of desired and undesired acidic compounds may be treated with a basic material of the character described.

Let it be assumed, for instance, that a hydrocarbon mixture containing desired acids of the R-COOH type and undesired acidic compounds of the R-OH type is contacted with an aqueous solution of ammonia. The desired acids combine with the ammonia to form watersoluble soaps which dissolve in the aqueous phase; the phenols, however, because of their weaker acidic character, do not undergo this reaction and remain as free phenols in the oil phase. The two phases are separated and the aqueous phase is subjected to distillation. Under the influence of the temperature attained during distillation the ammonium soaps are decomposed, yielding free ammonia and simultaneously releasing the organic acids. The ammonia is recovered by absorption in water in any suitable absorber, such as a packed tower, and may thus be reused repeatedly. The distillation may be discontinued, if desired, when the ammonia has been substantially removed, and the acids remaining in the still may then be separated from the remaining water and dried if desired. Optionally the distillation may be carried to a degree where the water and ammonia are both removed, leaving the acids in a dry condition. At this point the acids are ordinary dark colored liquids, the appearance of which can be greatly enhanced by continuing the distillation, using vacuum with or without steam if desired, after the water and ammonia are removed, thereby recovering the acids as a separate overhead cut or fraction. Obviously, the distillation of the acids may be performed in the same still as that used for ammonia distillation or, preferably, such distillation may be performed in a second still or series of stills.

Crude petroleum from any source, or any of its fractions, whether or not previously treated with acid or solvents, may be used as a source of the desired organic acids. Likewise, liquid hydrocarbon material of any nature, containing fatty acids, may be subjected to the process of the invention to extract the fatty acids therefrom. Fractions obtained from California crude petroleum, being relatively rich in organic acidity, comprise excellent material for the recovery of desired acids. Although the organic acids from all petroleum fractions are valuable products and are amenable to recovery by this process, the lower viscosity fractions, such as gas-oil fractions, comprise a preferred material to be treated. This preference is due to the fact that low viscosity oils separate more rapidly from the ammoniacal soap solutions and are more easily treated with the ammonia solution. In treating heavier lubricating oil fractions it is necessary to allow for longer settling times or to accelerate separation by centrifuging, but it should be understood that the scope of the invention is not limited to the treatment of any particular material or fraction thereof.

The strength of aqueous ammonia solution may vary within the scope of our invention from a dilute solution of the order of 4% up to a solution saturated with ammonia under superatmospheric pressure, and the quantity of ammonia solution used may vary from that containing just

sufficient ammonia to neutralize the desired acids up to large excesses of ammonia. It is preferable however, to treat the petroleum, or fraction, with a solution containing from 4% to 30% by weight of ammonia, in quantities corresponding up to 1000% excess. The use of such a large excess is advisable for two reasons. First, it provides sufficient aqueous phase for proper separation. Second, it insures complete extraction of the organic acids. In general, the use of solutions more dilute than 4% ammonia usually results in excessive emulsification.

If desired, an emulsion breaker, such as methyl or ethyl alcohol, acetone, or a saturated solution of a salt such as sodium chloride, may be incorporated in the ammonia solution or added to the mixture of oil and ammonia solution before or after agitation, or even after partial settling. Such an emulsion breaker may be desirable to reduce the time necessary for complete separation or to obtain the recovered organic acids less contaminated with hydrocarbons. Although ammonia solutions have been described above as the treating agent of our process, the process also contemplates the use of volatile amines, such as the lower alkyl amines, ethyl or methyl amines, or ethylene diamine, which have the necessary alkalinity to combine with the naphthenic or fatty acids and yet are sufficiently weak bases that the soaps may be hydrolyzed and the amines separated by distillation. Alkylol amines, such as monoethanolamine, diethanolamine, triethanolamine, propanolamine, iso-propanolamine and similar compounds may be used. Diethanolamine and triethanolamine are less desirable due to their high boiling points and tendency to form emulsions.

The following examples illustrate practice of the invention in a pilot plant and are given merely as illustrations.

#### EXAMPLE 1

25 gallons of gas oil were contacted with 1 gallon of 10% ammonia in aqueous solution at atmospheric temperature. The mixture was allowed to settle over night whereupon the contents of the agitator were found to be stratified into essentially two layers, with a very small interphase emulsion between. The lower aqueous portion was withdrawn, charged to a still, and distilled under atmospheric pressure to a degree sufficient to drive off most of the water. The vapors which come off in this operation were condensed in a water-cooled condenser and absorber and the condensate contained the recovered aqueous ammonia. The residue from this distillation consisted substantially of organic acids resulting from the decomposition of the water soluble soap solution. The organic acids recovered were free of phenols which remained in the upper oil layer.

The gas oil used in the above example was obtained from a Central California crude oil, commonly known to the trade as Coalinga Crude, and had the following properties:

Table 1

Gravity	26.0° A. P. I.	
Viscosity	47 sec. S. U. @ 100° F.	
A. S. T. M. distillation:		
I. B. P.	469° F.	
10%	504° F.	
50%	556° F.	
90%	660° F.	
95%	669° F.	
E. P.	730° F.	

From the above treatment of this gas oil the following yield of organic acids was obtained.

Table 2

5	Yield of crude acids.....	0.8% of the acid oil
	Analysis of crude acids:	
	Hydrocarbons.....	38.0%
	Acidic substance.....	62.0%
	Analysis of acidic substances:	
10	Naphthenic acids.....	100.0%
	Phenolic compounds.....	0.0%
	Equivalent weight of naphthenic acids.....	277 (by titration)
15	Yield of naphthenic acids.....	0.5% of acid oil

EXAMPLE 2

The treatment in Example 1 was repeated with the exception that the extracting agent used was 1 gallon of alcoholic-aqueous ammonia having the following compositions:

Ammonia .....	10%
Water .....	68%
Ethyl alcohol.....	22%

In this case the separation of the soap layer occurred rapidly, and was complete without the interphase emulsion noted in Example 1.

The alcohol was found to be substantially in the aqueous phase and was recovered with the ammonia. By this treatment the amount of hydrocarbon contamination of the naphthenic acids was reduced, as seen from the following:

Table 3

35	Yield of crude acids.....	0.8% of acid oil
	Analysis of crude acids:	
	Hydrocarbons .....	28%
	Acidic substances.....	72%
40	Analysis of acidic substances:	
	Naphthenic acids.....	100%
	Phenolic compounds .....	0%
	Equivalent weight of naphthenic acids.....	270
45	Yield of naphthenic acids.....	0.58%

To test the efficiency of the extraction of the organic acids by the use of this process, as compared to the conventional use of sodium hydroxide, 25 gallons of the gas oil were agitated with 1 gallon of 0.3% sodium hydroxide solution. After settling 16 hours, the alkaline soap layer was separated and acidified with an excess of sulfuric acid. The yield of naphthenic acids obtained was as follows:

Table 4

55	Yield of crude acids.....	0.88% of acid oil
	Analysis of crude acids:	
	Hydrocarbons .....	28%
	Acidic substances .....	72%
60	Analysis of acidic substances:	
	Naphthenic acids .....	96%
	Phenolic compounds.....	4%
	Equivalent wt. of naphthenic acids .....	277
65	Yield pure naphthenic acids.....	0.62%

From the above examples it is evident that by the practice of our invention it is possible to selectively obtain naphthenic acids substantially free from phenolic compounds by a simple extraction.

If it is desired to obtain naphthenic acids free from the entrained hydrocarbons, use may be made of their difference in volatility. For example, a laboratory fractionation conducted in a

vacuum still, using a 500 ml. "Pyrex" distilling flask with a three inch length of 1/4" by 1/4" prym ring packing in the neck, yielded the following figures for the hydrocarbon content of successive 10% cuts.

Charging stock: 200 ml. of crude acids substantially free from phenolic compounds and containing 28% hydrocarbon matter.

Table 5

Fraction	Percent hydrocarbon	Fraction	Percent hydrocarbon	Fraction	Percent hydrocarbon
0-10.....	96	30-40.....	21	60-70.....	0
10-20.....	75	40-50.....	10	70-80.....	0
20-30.....	40	50-60.....	4	80-93.....	0

With the highly efficient fractionation possible in industrial scale equipment, a sharper separation is easily obtainable.

EXAMPLE 3

As a further example of similarly treating a gas oil containing naphthenic acids of average molecular weight about 290, the oil was treated with 4% by volume of ammonia of varying concentrations, and also with 4% ethylene diamine.

The results are as follows:

Table 6

Extractant	Yield of crude acids	Percent of phenolic compounds in acids	Yield on oil of naphthenic acids
	Percent	Percent	Percent
28% NH <sub>3</sub> .....	67	0.0	0.56
25% NH <sub>3</sub> .....	56	0.0	0.47
20% NH <sub>3</sub> .....	56	0.0	0.47
60.7% ethylene diamine.....	55	0.0	0.46

Similarly, a treatment with 6% of a 100% monoethanol amine yielded 55% of crude acids giving a yield of 0.48% naphthenic acids and no phenolic compounds in the said acids.

At the lower percentage treating rates of about 4%, due to the low concentration of basic material, complete recovery of the acids is not possible and a certain percentage of the acids will remain in the oil either as free acids, or soaps, or both, from which the soaps may be recovered by further washing, or repeated washing with basic material, if the object is to completely purify the oil.

However, it is generally more desirable to use a percentage of basic material and a concentration thereof sufficient to recover a high percentage of acids, irrespective of whether the object is to purify the oil or simply to selectively recover organic acids.

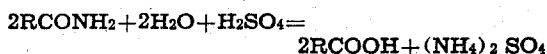
Any hydrocarbons contained in the crude acids recovered may easily be removed by well known methods.

While the above descriptions refer to a batch process, the method is readily capable of execution in a continuous system. For this purpose satisfactory types of continuous extractors and stills will be readily apparent to one skilled in the art.

With heavier streams, emulsion difficulties may be encountered and under such cases the extraction is successfully carried out under conditions of high temperature in a closed system, under elevated pressure. With the more viscous streams, many systems for using packed towers in countercurrent continuous treatment are available to insure proper contact between the

acid oil and the aqueous ammonia and to prolong the time of contact.

When the treatment is carried on at elevated temperatures for the purpose of reducing emulsion difficulties, care should be taken to maintain the lowest temperature which will bring about the desired reduction in viscosity of the oil. At elevated temperatures, particularly above 80° C., ammonia has a tendency to react with organic acids to form acid amides. These acid amides, if present, would not be decomposed during the subsequent distillation of the process but would remain dissolved in the extracted acids. When thus contaminated, the extracted acids require treatment with mineral acid to decompose the acid amides according to the following equation:



The formation of acid amides should therefore be avoided not only to avoid the inconvenience of further treatment, but also because the formation of the inorganic ammonium salt (ammonium sulfate in the above equation) represents a loss of ammonia as well as mineral acid.

It should also be borne in mind that, as the temperature is increased, the equilibrium of the reaction is displaced in a direction unfavorable to soap formation, and consequently low temperatures are desirable when practicable. Atmospheric temperatures, or lower, are most suitable for the reaction and, consequently, it is at times preferable to dilute viscous oils with non-viscous solvents, such as for example naphtha or gas oil, than to use high temperatures to reduce the viscosity. However, in other cases, treatment at temperatures as high as 60° to 80° C. may prove advantageous.

In the foregoing description and examples it has been shown how ammonia or its derivatives may be used to selectively extract the stronger organic acids free from weakly acidic phenolic compounds. The invention contemplates, moreover, the separation of stronger acids, readily reactive with weak volatile bases, from all types of weakly acidic substances, of which there are a great number present in petroleum. For example, naphthenic acids can be successfully separated from a petroleum fraction containing undesired mercaptans using ammonia as an extractant.

The invention also contemplates the purification of organic acids which are contaminated with organic matter such as hydrocarbons, phenols, and the like. By first diluting the organic acids with a suitable solvent, for example, with a light oil, organic acids in substantially pure form may be obtained by the process.

This application is a continuation-in-part of our copending application Serial Number 155,562, filed July 24, 1937.

We claim:

1. The process of separating organic acids from oily material containing the same, which comprises: treating said oily material containing organic acids with a basic reagent of higher volatility than said acids whereby soaps are formed and at a temperature below that at which amides tend to be formed, separating said soaps from said oily material, then dissociating said soaps by distillation to separately recover the organic acids and basic reagent.

2. The process according to claim 1 in which the basic reagent is ammonia.

3. The process according to claim 1 in which

the basic reagent is a soap forming organic derivative of ammonia.

4. The process according to claim 1 in which the basic reagent is alkylamine.

5. The process according to claim 1 in which the basic reagent is an alkylamine.

6. The process according to claim 1 in which the basic reagent is ammonia in aqueous solution between about 4% and 30% by volume of the oily material.

7. The process of separating organic acids from oily material containing the same, which comprises: treating a petroleum distillate containing naphthenic acids with a basic reagent of higher volatility than said acids whereby soaps are formed and at a temperature below that at which amides tend to be formed, separating said soaps from said oily material, then dissociating said soaps by distillation to separately recover the organic acids and basic reagent.

8. The process of separating organic acids from oily material containing the same, which comprises: treating said oily material containing organic acids with a basic reagent of higher volatility than said acids together with sufficient alcohol to prevent substantial emulsification whereby soaps are formed and at a temperature below that at which amides tend to be formed, separating said soaps from said oily material, then dissociating said soaps by distillation to separately recover the organic acids and basic reagent.

9. The process of selectively recovering organic acids from petroleum hydrocarbons which comprises: treating petroleum hydrocarbons containing organic acids of the R-COOH type and R-OH type with from about 4% to 30% by volume of a basic amino reagent of higher volatility than said acids whereby said R-COOH type acids alone are saponified, removing said saponified product from said hydrocarbons, then distilling said product to separately recover said basic reagent and said acids.

10. The process of recovering organic acids from petroleum hydrocarbons which comprises: treating petroleum hydrocarbons containing naphthenic acids and phenols with from about 4% to 30% by volume of aqueous ammonia to selectively saponify said naphthenic acids, separating the soaps formed as an aqueous solution, then fractionally distilling said solution to separately recover an aqueous solution of ammonia and said naphthenic acids.

11. The process of selectively recovering organic acids from oily material containing the same, which comprises: treating a petroleum distillate containing relatively strong organic acids and relatively weakly acidic organic compounds with a basic reagent of higher volatility than said stronger acids whereby soaps are formed, separating said soaps from said distillate, then dissociating said soaps by distillation to separately recover said stronger acids and said basic reagent.

12. The process according to claim 1 in which the basic reagent is an aqueous solution of a soap forming derivative of ammonia.

13. The process according to claim 1 in which the basic reagent is an aqueous solution of an alkylamine.

14. The process according to claim 1 in which the basic reagent is an aqueous solution of an alkylamine.

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CERTIFICATE OF CORRECTION.

Patent No. 2,186,249.

January 9, 1940.

ARTHUR LAZAR, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 7, for "8-OH" read R-OH; page 2, first column, line 34, for the word "ordinary" read ordinarily; line 37, for "vaccum" read vacuum; page 3, first column, line 18, after "treatment" insert given; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 5th day of March, A. D. 1940.

(Seal)

Henry Van Arsdale,  
Acting Commissioner of Patents.