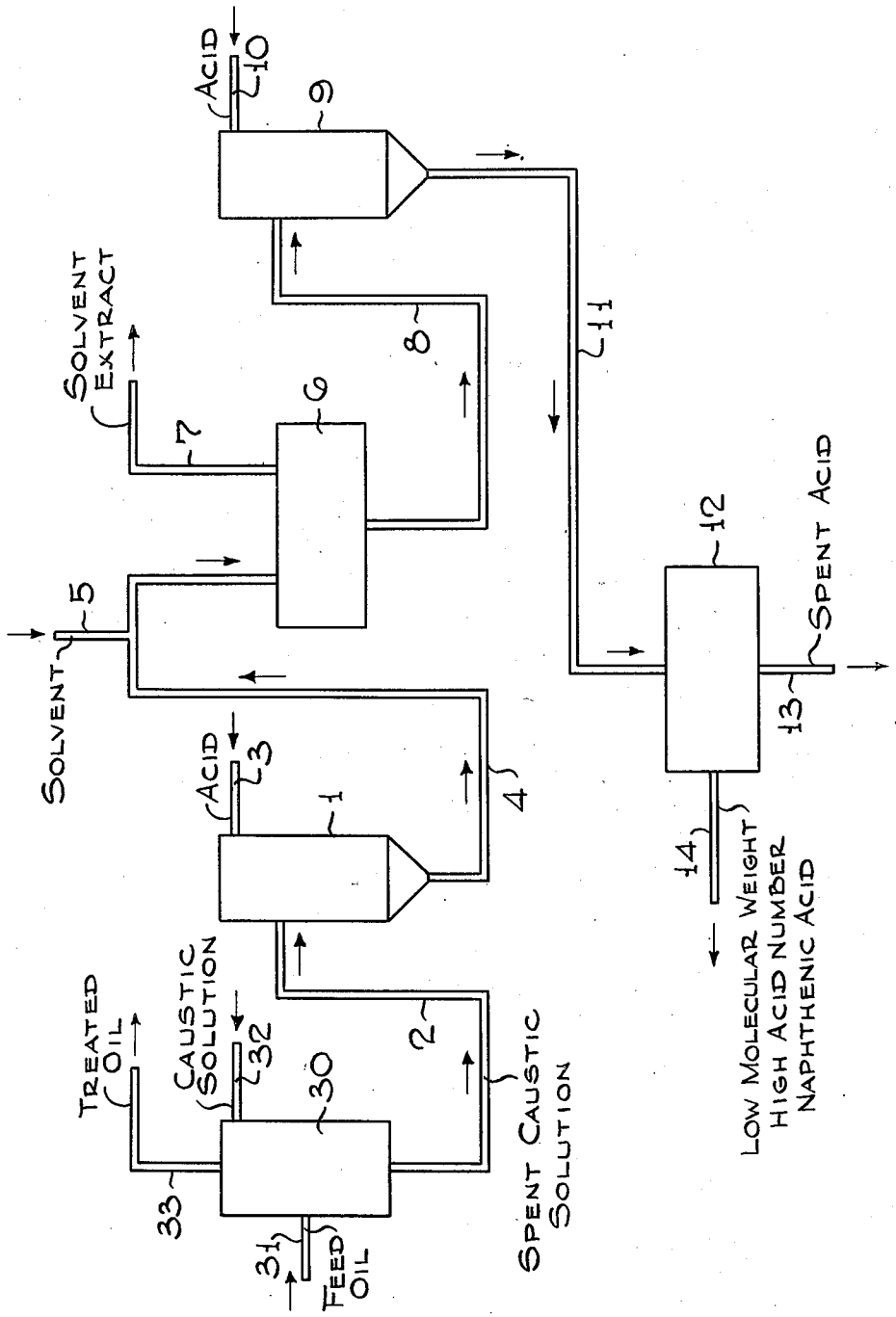
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PROCESS FOR THE RECOVERY AND PURIFICATION OF NAPHTHENIC ACIDS

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PROCESS FOR THE RECOVERY AND PURIFICATION OF NAPHTHENIC ACIDS

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1

The present invention relates to a process for the separation and purification of naphthenic acids found in petroleum oils. The invention is more particularly concerned with the production of high yields of high quality low molecular weight naphthenic acids which are suitable for use in paints as driers. In accordance with the present invention petroleum oils containing relatively high and relatively low molecular weight naphthenic acids are treated with a caustic solution in order to remove these acids. The caustic solution is then treated in an initial stage with a suitable reagent in order to partially regenerate a portion of the naphthenates. The relatively high molecular weight naphthenic acids regenerated in the initial stage are removed along with unsaponificable oily constituents. The relatively low molecular weight naphthenates are then completely regenerated in a second stage to produce high yields of low molecular weight naphthenic acids suitable as paint driers and the like.

It is well known in the art to segregate naphthenic acids from petroleum oils containing the same. For example, one method is to treat a petroleum oil fraction with a caustic or equivalent reagent to form the corresponding naphthenates. The naphthenic acids are then regenerated by treating the naphthenates with sulfuric acid. The resulting crude naphthenic acids containing unsaponifiable oily constituents are then subjected to a distillation operation wherein the oily constituents are segregated from the desired fractions of naphthenic acids. This method is not entirely satisfactory for the production of high quality naphthenic acids particularly when it is desired that these acids have an acid number above about 240 and be relatively free of unsaponifiable oily constituents. In accordance with the present invention, high quality naphthenic acids in good yields are obtained. The invention may be readily understood by referring to the drawing illustrating an embodiment of the same.

Referring specifically to the drawing, a feed petroleum oil which for the purpose of illustration is assumed to be a gas oil boiling in the range from about 400°–750° F. is introduced into treating zone 30 by means of feed line 31. A caustic solution is introduced into zone 30 by

2

means of line 32. The treated oil is withdrawn from zone 30 by means of line 33 and further refined as desired. Usually this stream is passed to a cracking operation. The spent caustic phase is withdrawn from zone 30 by means of line 2 and introduced into an initial regeneration stage 1. In this stage, the spent caustic solution is contacted under controlled conditions with an acid which for the purpose of illustration is assumed to be a 98% sulfuric acid. The acid is introduced into initial stage 1 by means of line 3. Sufficient acid is introduced to convert approximately 10% of the naphthenates to their corresponding naphthenic acids.

The partially treated naphthenic acids and naphthenates along with unsaponifiable oily constituents are removed from zone 1 by means of line 4 and introduced into settling zone 6. Prior to introducing the stream into zone 6, a solvent for the naphthenic acids is introduced into line 4 by means of line 5. For the purpose of illustration it is assumed that the solvent comprises ether containing from about 3–6 carbon atoms in the molecule. In zone 6 an ether phase containing naphthenic acids and unsaponifiable oily constituents forms as well as a naphthenate phase. The solvent extract phase is withdrawn from zone 6 by means of line 7 and may be handled in any manner desirable to segregate the high molecular weight naphthenic acids and the oily constituents.

The naphthenate phase containing relatively low molecular weight constituents is withdrawn from zone 6 by means of line 8 and introduced into a secondary regeneration stage 9. Sulfuric or an equivalent acid is introduced into stage 9 by means of line 10 under conditions to completely convert the remaining naphthenates to corresponding naphthenic acids. The solution is withdrawn from the bottom of stage 9 by means of line 11 and introduced into settling zone 12 wherein the spent acid is segregated and removed by means of line 13. The naphthenic acid phase of a relatively high purity and substantially completely free of oily constituents is removed from zone 12 by means of line 14.

As pointed out heretofore, the present invention is concerned with a two-stage regeneration process for the recovery of naphthenic acids. The invention is particularly adapted for the

treatment of petroleum oils boiling in the general range from about 400°–900° F. Also, as pointed out heretofore, it is desirable that these naphthenates if they are to be used as driers in paints must have an acid number of not less than about 240. Furthermore, if the process is to be successful the yield of the high quality naphthenic acids must be high.

The naphthenic acids present in petroleum oils have molecular weights varying appreciably, as for example, in the range from about 160 to 360 and higher. The acid numbers of these naphthenic acids likewise vary appreciably, as for example, in the range from about 30 to 300. These acid numbers are a function of the acid molecular weight and the unsaponifiable oil content. The high molecular weight naphthenic acids have been a greater solubilizing action on the unsaponifiable oils than the lower molecular weight acids. Naphthenic acids having a molecular weight in the range from about 180 to 275 have exhibited acid numbers in a descending range from about 312 to 204. Therefore, the higher the molecular weight and the unsaponifiable oil content, the lower the acid number.

The reagent used to generate the naphthenates in the respective stages preferably comprises sulfuric acid or carbon dioxide. If sulfuric acid is employed it is preferred that the concentration of the acid be in the range from about 95 to 100%. If carbon dioxide is employed, it may be employed as such or the caustic extract may be treated with gas containing carbon dioxide. In general, atmospheric temperatures and pressures are employed in the acidification stages.

The present invention may be readily understood by the following examples illustrating the same.

EXAMPLE I

A petroleum oil boiling in the range from about 400°–750° F. and secured from a Venezuelan crude was contacted with a 6 Bé. sodium hydroxide solution. The spent caustic was segregated into various portions and acidified in two stages with 95% to 98% sulfuric acid. In an initial run, one portion was completely acidified in a single stage. In 4 subsequent runs a two-stage operation was employed wherein the extent to which the naphthenates were acidified in the initial stages was varied from 5% to 30%. The results of these runs are tabulated below.

Table I

SINGLE STAGE ACIDIFICATION

RUN #1

Acid No.[1]	219
Aver. mol. weight of acids	225
Mols acid	87.9
Mols oil	12.1
Per cent oil in acid	12.1

TWO-STAGE ACIDIFICATION

	First Stage, Naphthenic Acid Regeneration	Second Stage, Naphthenic Acid Regeneration
RUN #2		
5% Initial Liberation:		
Acid No	31	231
Aver. Mol. Weight of Acids	272	223
Mols Acid	4.4	83.5
Mols Oil	3.7	8.4
Mol Per Cent Oil in Acid	45.7	9.15
Yield:		
Mol Per Cent Acid	5	95
Weight Per Cent Acid	10	90

Table 1—Continued

TWO-STAGE ACIDIFICATION—Continued

	First Stage, Naphthenic Acid Regeneration	Second State, Naphthenic Acid Regeneration
RUN #3		
10% Liberation:		
Acid No	50	240
Aver. Mol. Weight of Acids	270	222
Mols Acid	8.8	79.1
Mols Oil	6.7	5.4
Mol Per Cent Oil in Acid	43.3	6.4
Yield:		
Mol Per Cent Acid	10	90
Weight Per Cent Acid	18	82
RUN #4		
20% Liberation:		
Acid No	107	247
Aver. Mol. Weight of Acids	262	220
Mols Acid	17.6	70.3
Mols Oil	8.8	3.3
Mol Per Cent Oil in Acid	33.2	4.5
Yield:		
Mol Per Cent Acid	20	80
Weight Per Cent Acid	29.4	70.6
RUN #5		
30% Liberation:		
Acid No	142	255
Aver. Mol. Weight of Acids	259	214
Mols Acid	26.4	61.5
Mols Oil	9.1	3.0
Mol Per Cent Oil in Acid	25.6	4.7
Yield:		
Mol Per Cent Acid	30	70
Weight Per Cent Acid	40.1	59.9

It is to be observed that in runs #2 to #5 the unsaponifiable oils are present in a very high concentration with the naphthenic acids segregated in the initial stage. It is also to be observed that in runs #3 to #5 the acid number of the product secured in the second stage is 240 or better. However, with respect to runs #4 and #5 the yields dropped off appreciably (weight per cent) as compared to the results secured in run #3. It is therefore apparent that if a naphthenic acid is to be produced which has an acid number in excess of 240, it will be necessary to liberate from 10 to 30 mol. per cent of the naphthenic acids in an initial stage and thus remove unsaponifiable oily constituents therewith. It is also apparent that if good yields are to be obtained when treating a gas oil boiling in the range from about 400°–750° F., the extent of the acidification in the initial stage should be in the range from about 10 to 20%.

EXAMPLE II

A petroleum oil boiling in the range from about 600°–900° F. and secured from a Venezuelan crude was contacted with a 6 Bé. sodium hydroxide solution. The spent caustic was segregated into various portions and acidified in two stages. In an initial run one portion was completely acidified in a single stage. In 4 subsequent runs a two-stage operation was employed wherein the extent to which the naphthenates were acidified in the initial stages was varied from 40 to 70%. The results of these runs are tabulated below.

Table II

SINGLE STAGE ACIDIFICATION

RUN #1

Acid No.[1]	166
Aver. mol. weight of acids	270
Mols acid	79.6
Mols oil	20.4
Per cent oil in acid	20.4

[1] Acid No.—Number of mgs. of KOH required to neutralize 1 gram of acid.

Table II—Continued

TWO-STAGE ACIDIFICATION

	First Stage, Naphthenic Acid Regeneration	Second Stage, Naphthenic Acid Regeneration
RUN #2		
40 Per Cent Liberation:		
Acid No.	96.8	228
Aver. Mol. Weight of Acids	325	235
Mols Acid	31.6	48
Mols Oil	13.9	6.5
Mol Per Cent Oil in Acid	30.6	11.9
Yield:		
Mol Per Cent Acid	40	60
Weight Per Cent Acid	56.4	43.6
RUN #3		
50 Per Cent Liberation:		
Acid No.	112	238
Aver. Mol. Weight of Acids	315	227
Mols Acid	39.8	39.8
Mols Oil	14.7	5.7
Mol Per Cent Oil in Acid	26.9	12.5
Yield:		
Mol Per Cent Acid	50	50
Weight Per Cent Acid	65.2	34.8
RUN #4		
60 Per Cent Liberation:		
Acid No.	124	250
Aver. Mol. Weight of Acids	307	217
Mols Acid	47.8	31.8
Mols Oil	15.3	4.9
Mol Per Cent Oil in Acid	24.2	13.4
Yield:		
Mol Per Cent Acid	60	40
Weight Per Cent Acid	73.6	26.4
RUN #5		
70 Per Cent Liberation:		
Acid No.	140	263
Aver. Mol. Weight of Acids	289	208
Mols Acid	55.7	23.9
Mols Oil	15.6	4.8
Mol Per Cent Oil in Acid	21.9	16.7
Yield:		
Mol Per Cent Acid	70	30
Weight Per Cent Acid	81.1	18.9

The data illustrated in Table II, runs #2 to #5, show a very high concentration of unsaponifiable oils segregated with naphthenic acids in the initial stage. The acid number of the product secured in the second stage with respect to runs #3 to #5 is about 238 or better. However, with respect to runs #4 and #5 the yields drop off appreciably (weight per cent) as compared to the results secured in run #3. It is therefore apparent that if a naphthenic acid is to be produced which has an acid number in excess of 238, it will be necessary to liberate from 50 to 70 mol. per cent of the naphthenic acids in an initial stage and thus remove unsaponifiable oily constituents therewith. It is also apparent that if good yields are to be obtained when treating a gas oil boiling in the range from about 600°–900° F., the extent of the acidification in the initial stage should be in the range from about 50 to 60%.

EXAMPLE III

The naphthenic acids produced in run #1 of Example I were subjected to distillation and 3 fractions segregated, the results are as follows:

Table III

SINGLE STAGE ACIDIFICATION

Acid No.	219
Aver. mol. weight of acids	225
Mols acid	87.9
Mols oil	12.1
Per cent oil in acid	12.1

Table III—Continued

DISTILLATION OF SINGLE STAGE ACIDIFICATION PRODUCT FRACTIONS

	#1	#2	#3
Acid No.	217	234	180
Aver. Mol. Weight of Acids	167	225	305
Mols Acid	12.07	64.66	11.17
Mols Oil	7.53	4.34	0.23
Mol Per cent Oil in Acid	38.4	6.3	2.0
Yield:			
Mol Per cent Acid	13.8	73.5	12.7
Weight Per cent Acid	10.0	72.9	17.1

It is to be observed that fraction #2 exhibits an appreciable drop in yield (weight per cent acid) when compared to the product yield secured in the second stage of run #2, Table I, Example I. In order to obtain naphthenic acids having an acid number of 240 or better in a distillation process, it requires closer fractionating of the acidified naphthenates. The yield (weight per cent acid) would be considerably lower than that shown for fraction #2.

EXAMPLE IV

The extent to which unsaponifiable oil will affect the acid number is readily apparent from the following test data. A naphthenic acid fraction boiling in the range from 400°–750° F. has naphthenic acids the molecular weights of which vary from 180 to 275. The respective acid numbers vary from about 312 to 204. If this fraction should contain about 10% of unsaponifiable oily constituents, the acid number would be about 184.

What is claimed is:

1. Process for the segregation of low molecular weight naphthenic acids of high quality from petroleum oils containing the same, which comprises washing a feed petroleum oil containing relatively high and relatively low molecular weight naphthenic acids with a caustic solution, separating the respective oil and caustic phases, treating said separated caustic phase in an initial regeneration stage with a reagent adapted to convert at least 10% of the relatively high molecular weight naphthenates into their correspondingly high molecular weight naphthenic acids, extracting the relatively high molecular weight naphthenic acids with a suitable solvent, whereby the relatively high molecular weight naphthenic acids and unsaponifiable oil constituents are dissolved in said solvent, separating the solvent extract phase from the relatively low molecular weight naphthenate phase, and thereafter in a second stage completely regenerating the relatively low molecular weight naphthenates with a suitable reagent whereby high quality low molecular weight naphthenic acids substantially completely free of unsaponifiable oil constituents are secured.

2. Process as defined by claim 1 wherein said feed petroleum oil boils in the range from about 400° F. to about 750° F. and wherein said caustic phase is treated in said initial regeneration stage under conditions to regenerate from 10 to 30% of said naphthenates.

3. Process as defined by claim 1 wherein said feed petroleum oil boils in the range from about 600° F. to about 900° F. and wherein said caustic phase is treated in said initial stage under conditions to regenerate from about 50% to 70% of the naphthenates.

4. Process for the production of high yields of low molecular weight naphthenic acids having an acid number of at least 240 from a petroleum oil boiling in the range from about 400° F. to 750° F.

which comprises washing said petroleum oil with a caustic solution, separating the caustic phase from the treated oil, treating said caustic phase in an initial regeneration stage with a reagent adapted to convert at least 10% of the naphthenates into corresponding naphthenic acids, treating the solution with a solvent to remove the naphthenic acids and entrain unsaponifiable constituents, removing the solvent extract and treating the remaining naphthenates in a secondary stage under conditions to convert the same to corresponding naphthenic acids, whereby high yields of high quality naphthenic acids are secured.

5. Process for the production of high yields of low molecular weight naphthentic acids having an acid number of at least 240 from a petroleum oil boiling in the range from about 600° F. to 900° F. which comprises washing said petroleum oil with a caustic solution, separating the caustic phase from the treated oil, treating said caustic phase in an initial regeneration stage with a reagent adapted to convert about 50% of the naphthenates into corresponding naphthenic acids, treating the solution with a solvent to remove the naphthenic acids and entrain unsaponifiable constituents, removing the solvent extract and treating the remaining naphthenates in a secondary stage under conditions to convert the same to corresponding naphthenic acids, whereby high yields of high quality naphthenic acids are secured.

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