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PROCESS FOR PURIFYING NAPHTHENIC ACIDS

Raymond C. Rich and Curtis W. Cannon, Houston, Tex., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

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This invention relates to a method for refining naphthenic acids by treating same in the liquid phase with a heavy metal oxide having a high affinity for sulfur, at a temperature between about 300–450° F. It is preferred to apply the treatment to aqueous solutions of alkali metal naphthenates rather than to the free naphthenic acids, and to blow steam, air, or both through the mixture while treating. After completing the treatment, the naphthenic soap or free acid is washed with aqueous sulfuric or similar acid.

Naphthenic acids are produced largely by extracting natural unrefined mineral oils containing same with alkaline reacting oil-insoluble liquids, and acidifying the extract to liberate extracted naphthenic acids. Naphthenic acids so obtained normally contain large proportions of impurities, chiefly neutral oils and sulfur compounds. These impurities greatly reduce the commercial value and usefulness of the naphthenic acids by reason of lowering their neutralization number and by forming dark, unstable, heavy metal salts, such as the lead salts; heavy metal salts of naphthenic acids are used as paint driers, extreme pressure compounds in mineral lubricating oils, adhesives, and for many other purposes.

It is a purpose of this invention to provide a simple refining process, whereby from impure naphthenic acids refined acids are produced having high neutralization numbers and capable of forming light-colored heavy metal salts, in particular lead salts which do not turn black upon preparation or standing. Other purposes and advantages will become evident from the following description of our process.

Our preferred method is as follows:

An aqueous solution of alkali metal naphthenates such as may be produced by extracting mineral oils containing naphthenic acids with aqueous solutions of alkali metal hydroxides, or by dissolving impure free naphthenic acids in aqueous caustic alkali, etc., is heated in a suitable vessel such as a shell still, cone bottom tank equipped with overhead vapor line and condenser, etc., preferably at substantially atmospheric or lower pressures to a temperature between about 300–450° F. In the course of this heating water of solution may be vaporized, and the naphthenic soap solution may be concentrated materially. An inert gas or vapor is blown through the liquid soap, preferably after the latter has reached approximately the desired treating temperature, in order to strip neutral oils from the soap solution. Spent stripping gas may be cooled in a condenser to separate therefrom liquefiable matter and to recover the neutral oils which it contains. Since the naphthenates are substantially non-volatile as long as they are at least slightly alkaline, i. e., their pH value is above about 7, a good separation of neutral oils from the naphthenic acids can be achieved in this manner without noticeable loss of acids. Suitable stripping gases are those which are substantially inert to naphthenic acids under the conditions of the stripping, such as steam, air, flue gases, hydrocarbon gases, etc. Steam or air or both are normally preferred as being the least expensive and most readily available.

The time required for the stripping may vary over a wide range. It may be sufficient to blow for 10 or 15 minutes, or it may be necessary to continue the blowing for 30 hours or longer, depending upon the temperature maintained during the blowing and the desired degree of freedom from neutral oils and harmful sulfur compounds. As a general rule, even at temperatures close to the upper temperature limit the time of blowing is normally 15 minutes or longer, whereas at a temperature close to 300° F., 15 hours of blowing is usually sufficient.

During, before or after the stripping, an amount of heavy metal oxide which has high affinity to sulfur is contacted with the soap at temperatures substantially the same as those suitable for the stripping. Suitable oxides are especially the lead and copper oxides, although other heavy metal oxides such as those of Fe, Ni, Co, Zn, Cd, etc., may also be used. In contact with the soap, sulfur compounds of a deleterious nature, e. g., mercaptans, and possibly other thiocompounds, react with the heavy metal oxide to form metallic sulphides and organic substances which are not detrimental and some of which may be removed by the stripping as described above. If air is used for blowing, at least a portion of the metal sulfides are normally converted to the sulfates, which may be soluble in or preferentially wetted by water. This may have a considerable advantage as will be shown later.

The temperature maintained during the stripping and treatment with the metal oxide should not be below about 300° F., since both the stripping and the removal of harmful sulfur compounds appear to be slow and incomplete at lower temperatures. On the other hand, no advantage is gained by operating at temperature above about 450° F., and on the contrary, colors of heavy metal naphthenates produced from naphthenic acids refined at temperatures above about 450° F. may be very poor and unstable. Temperatures between about 340°–425° F. appear to be most desirable.

As hereinbefore stated, we prefer to treat the alkali metal naphthenates rather than the free acids. However, the treatment with the metal oxide is effective through an extremely wide range of pH values of the naphthenates and naphthenic acids, respectively. For reasons explained before, we prefer to treat alkaline naphthenates so

as to enable simultaneously stripping without loss of naphthenic acids during the stripping. If desired, however, free naphthenic acids may be present, or, instead of treating naphthenic soaps, we may treat the free acids. This, however, has the disadvantage that neutral oils cannot be readily stripped from the naphthenic acids during the treatment, except at a material loss of the latter; and the improvement due to the treatment is more or less restricted to a conversion of harmful sulfur compounds to less harmful organic sulfides, unless the metal oxide treatment is preceded or followed by a separate stripping step applied to the naphthenic acid soaps. Stripping before treating with the metal oxide is capable of removing neutral oils but not all the harmful sulfur compounds which are altered during the subsequent metal oxide treatment; while stripping after the treatment may remove both. Thus, whereas separate stripping of the naphthenates and treatment of the free naphthenic acids with the metal oxide may result in satisfactory refinement of the naphthenic acids, such two step procedure is obviously more cumbersome, and, moreover, requires two washes with aqueous sulfuric acid, one for the liberation of naphthenic acids from the naphthenates and another one for the removal of the dark heavy metal salts formed in the treatment of the free naphthenic acids. In contrast, the simultaneous stripping and treating of the naphthenates requires but a single sulfuric acid wash for the liberation of naphthenic acids. Moreover, the amohnt of heavy metal oxide required to effect the removal of harmful sulfur compounds seems to be greater when treating the free naphthenic acids rather than the naphthenic soap.

On the other hand, the naphthenic soaps to be treated may contain considerable excess of free alkali. Such an excess is neither harmful nor beneficial for the removal of neutral oils and harmful sulfur compounds.

The amount of the heavy metal oxide required to effect the removal of harmful sulfur compounds sufficient to produce from the refined naphthenic acids light-colored stable heavy metal salts, is normally between about 5–10% by weight of the naphthenic acids, and usually less than 5% when treating the soap rather than the free acid. When, however, treating the free naphthenic acids with the heavy metal oxides, amounts required are frequently in excess of 5%. Within the above limitation, the requirements may vary a great deal, depending upon the type and amount of harmful sulfur compounds contained in the naphthenic acids.

After completed treatment as described above, solid matter such as heavy metal oxide and sulfide suspended in the treated material may be separated by any conventional method. This often meets with some difficulty, and it is therefore advantageous to convert, if possible, the insoluble oxides or sulfides to water-soluble or preferentially wetted sulfates which can later be separated from the naphthenic acids by simple water washes. The resulting naphethenic soap or acid is then acidified with an aqueous solution of a suitable mineral acid which is stronger than the naphthenic acids, such as sulfuric, hydrochloric, etc., acids to liberate the naphthenic acids from the soaps and/or heavy metal naphthenates which are formed when the free naphthenic acids are treated with the metal oxide, as the case may be. Liberated naphthenic acids are separated from the resulting aqueous layer, and are washed with water to remove free mineral acid and salts. The washed naphthenic acids may now be used after distillation for preparing the desired light colored heavy metal salts such as lead, cobalt, copper, etc., naphthenates, which are useful for many purposes. If desired, the purified naphthenic acids may be fractionally distilled to produce several grades of the desired naphthenates.

The following example further illustrates our invention:

Raw naphthenic acids produced by extracting mineral oil containing same with aqueous NaCH, acidifying the extract with dilute aqueous sulfuric acid, separating the liberated naphthenic acids from the resulting aqueous layer and washing the separated naphthenic acids with water to remove mineral salts and acids, had a neutralization number of 131 and a sulfur content of .96%. The acids were distilled to take overhead two separate 30% fractions which had neutralization numbers of 48 and 142, respectively. Lead soaps produced with the distilled fractions were black and of 13 color on the Gardner Color Standards scale, respectively.

Portions of the above extract comprising sodium naphthenates were then treated according to our invention while simultaneously stripping under conditions and with the results shown in the tables below:

Treatment of extract

Run	Metal oxide		Treating conditions		
	Used for treating	Amount in percent of N. A.*	Temperature	Duration	Stripping medium
			° F.		
1	PbO	1	475	2 hours	Air.
2	PbO	3	375	15 min	Do.
3	CuO	3	375	do	Do.
4	PbO	3	400	1 hour	Steam.
5	PbO	3	300–340	16 hours	Steam and air.
6	None	None	300–340	30 hours	Steam.

* N. A.=naphthenic acids.

The treated extracts from the above six runs were separately acidified with dilute sulfuric acid, liberated naphthenic acids were separated from the resulting aqueous layers, and the separated naphthenic acids were washed with water to remove mineral salts and acids. Each of the purified naphthenic acids so obtained was fractionally distilled to separate two consecutive 30% overhead fractions which were then converted to their lead salts. The several products had the following properties:

Properties

Run	Sulfur content of undistilled naphthenic acids	Neutralization No.			Colors of lead salts in Gardner Color Standard	
		Of undistilled naphthenic acids	First fraction	Second fraction	First fraction	Second fraction
	Percent					
1	.59	207	222	215	9	9+
2		157	133	160	8+	8
3		169	142	186	8	8
4		155	131	169	8−	8
5		228	242	217	6+	7+
6		208	220	208	9−	11+

As will be noted, run 1, carried out at a temperature above 450° F., and run 6, restricted to steaming in the absence of a metal oxide, resulted in relatively dark colored lead salts.

Colors of the lead naphthenates in the above color scale are usually considered satisfactory as driers in paints when below about 9.

In another experiment, the above naphthenate extract was first blown with air for 15 minutes at 400° F. in the absence of a heavy metal oxide, and the blown extract was acidified with dilute aqueous sulfuric acid. Liberated naphthenic acids were separated from the aqueous layer, were washed with water and treated with 8% by weight cupric oxide at 385° F. for 30 minutes. The treated acids were again acidified and washed and the resulting product had a neutralization number of 166 and a sulfur content of .67. Two 30% distilled fractions of the purified naphthenic acids had neutralization numbers of 146 and 186, respectively, and colors of the lead salts of these overhead fractions were 6— and 7+, respectively. When treating the liberated naphthenic acids in the above manner but using 3% CuO instead of the above 8% CuO, lead naphthenates produced from similar distilled fractions of the resulting refined naphthenic acids had colors of 9.

We claim as our invention:

1. A process for refining naphthenic acids containing neutral oils and harmful sulfur compounds, comprising subjecting an aqueous solution of the alkali metal salts of said naphthenic acids to a simultaneous treatment with a heavy metal oxide having high affinity to sulfur and to a stripping operation by blowing with a stripping medium which is substantially inert to naphthenic acids under the conditions of the stripping, at a temperature between 300–450° F. and for a time sufficient to remove a substantial amount of said neutral oils, and reacting the treated and stripped naphthenate solution with a mineral acid which is stronger than naphthenic acids to liberate naphthenic acids from said naphthenate solution.

2. A process for refining naphthenic acids containing neutral oil and harmful sulfur compounds comprising subjecting an aqueous solution of the alkali metal salts of said naphthenic acids free from a substantial excess of free caustic alkali to a simultaneous treatment with a heavy metal oxide having high affinity to sulfur and to a stripping operation by blowing with a stripping medium which is substantially inert to naphthenic acids under the conditions of the stripping, at a temperature between 300–450° F. and for a time sufficient to remove a substantial amount of said neutral oils, and reacting the treated and stripped naphthenate solution with a mineral acid which is stronger than naphthenic acids to liberate naphthenic acids from said naphthenate solution.

3. A process for refining naphthenic acids containing neutral oils and harmful sulfur compounds, comprising subjecting the alkali metal salts of said acids in the liquid phase and at a temperature between 300–450° F. to a treatment with a heavy metal oxide having high affinity to sulfur and to a stripping operation by blowing with a stripping medium which is substantially inert to the naphthenates under the conditions of the stripping, at a temperature and for a time sufficient to remove a substantial portion of said neutral oils, and reacting the treated and stripped naphthenates with a mineral acid which is stronger than naphthenic acids to liberate naphthenic acids from the liquids.

4. The process of claim 3 in which the heavy metal oxide is lead oxide.

5. The process of claim 3 in which the heavy metal oxide is copper oxide.

6. A process for refining naphthenic acids containing neutral oils and harmful sulfur compounds, comprising subjecting an aqueous solution of the alkali metal salts of said naphthenic acids simultaneously to a treatment with a heavy metal oxide having high affinity to sulfur and to a stripping operation by blowing with a stripping medium which is substantially inert to naphthenic acids under the conditions of the stripping, at a temperature between 300–450° F. and for a time sufficient to remove a substantial amount of said neutral oils.

7. A process for refining naphthenic acids containing neutral oils and harmful sulfur compounds, comprising subjecting alkali metal salts of said acids in the liquid phase and at a temperature between 300° F. to 450° F. to a treatment with a heavy metal oxide having high affinity to sulfur and to a stripping operation by blowing with a stripping medium which is substantially inert to the naphthenates under the conditions of the stripping, at a temperature and for a time sufficient to remove a substantial portion of said neutral oils, separating the spent heavy metal oxide, and reacting the treated and stripped naphthenate solution with a mineral acid which is stronger than naphthenic acids to liberate naphthenic acids from the liquids.

RAYMOND C. RICH.
CURTIS W. CANNON.