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SOAP MANUFACTURE

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This invention relates to methods of manufacturing and separating certain types of soaps and their acids.

One object of the invention is the fractionation or separation of such soaps or their acids in order to obtain soaps of high molecular weight or of weak acids or such acids themselves, in a condition free from soaps of low molecular weight or stronger acids or free from such stronger acids with which the high molecular weight or weaker acids initially occur. Another object of the invention is to provide a means of producing certain soaps free from objectionable other soaps, such as soaps of inadequate oil solubility.

One aspect of the invention is the fractionation of soaps, or of acids from which soaps are formed, with respect to their solubility in various liquid carriers or selective solvents, for example, mineral oil and water, whereby acids which are freely soluble in the liquid carrier may be segregated from soaps or their acids not so freely soluble therein or soluble in another carrier, such as water.

In particular, this invention relates to the fractionation of soaps produced from synthetic acids obtained by the oxidation of petroleum fractions, such as slack waxes, deoiled waxes and other paraffin waxes, petrolatum, and lubricating oil fractions, especially highly refined, highly paraffinic lubricating oil fractions, such as heavily solvent-treated, paraffinic-type lubricating oils. The invention may be considered to constitute fractionation between high molecular weight acids and lower molecular weight acids, or between weaker and stronger organic acidic materials capable of forming soaps or salts, or between oil-soluble and oil-insoluble or water-soluble acidic materials, or between organic acidic materials respectively soluble and insoluble in selective solvents.

Stated briefly, the invention resides in the preparation of a mixture of soap-forming acids containing both low and high molecular weight acids of varying strengths, saponifying the entire batch with an excess of an alkali such as caustic soda, acidifying the saponification batch with a dilute strong mineral acid such as sulfuric acid or hydrochloric acid in amount to neutralize all of the excess caustic and to decompose the more easily hydrolyzed soap in order to "crack out" the proportion of water-insoluble weaker acids desired to be segregated, as has been previously determined by test, such liberated acids being then separated from the unconverted soaps of the other or stronger acids. The water-insoluble weaker acids may be collected in a layer of oil which may be present, the stronger acids remaining in soap form in aqueous solution. When the acids of the remaining soaps are desired for any purpose they also may be "cracked out" of the aqueous solution with additional mineral acid, and recovered. Where the water-insoluble acids are desired since these are set free by decomposition and float upon the surface of the acidified batch (in an oil layer if present), this layer may be drawn off and washed; where soaps thereof are desired the acids will then be converted into such soaps. The invention also includes this latter step of separating, washing and resaponifying the separated acid fractions.

Described in greater detail, one type of acidic material adapted to treatment according to the present invention is prepared by oxidizing suitable petroleum fractions such as the paraffin waxes, lubricating oil fractions or the like mentioned. This may be effected in any known or preferred manner as by charging the material into a stainless steel vessel or other appropriate oxidizing chamber, and blowing air therethrough at elevated temperatures such as 250° F. to 350° F. at any preferred rate for an adequate period of time to effect the desired degree of oxidation and consequent formation of mixed synthetic petroleum acids. Dependent upon the conditions of the oxidation, the petroleum fractions will be oxidized to a greater or lesser degree.

The oxidized mass from which acids are to be separated may contain or have added thereto a quantity of unsaponifiable oil such as mineral lubricating oil, in which the desired weak acids are soluble. This mass is then commingled with an excess of a suitable aqueous alkaline solution, for example, 100% excess of 20% caustic soda solution, to saponify the batch. Saponification is facilitated by heating or boiling the mass for a sufficient length of time to saponify the acidic materials to the desired degree. This operation may include saponification not only of acids but of esters, lactones and other materials convertible into soaps. After saponification of the oil mixture has been completed the batch may or may not be allowed to stand, as desired. If it is allowed to stand it may or may not stratify depending upon the extent and conditions of oxidation and saponification. Ordinarily, there is no need for stratification, and the whole batch is preferably diluted with a large volume of water, for example, five or ten times its volume.

The sodium soaps are soluble in the water. Dilute mineral acid such as sulfuric acid or hydrochloric acid or other acid capable of decomposing the soaps is then added in amount necessary to neutralize all the excess alkali and also to decompose the desired fraction or percentage of the soaps, and thereby release or "crack out" the desired acids. The amount of mineral acid required for this purpose is determined by test of the saponification batch. This may be determined by the trial and error method, or by obtaining acid or saponification number, or by water or oil solubilities, or molecular weights, or analysis for percentage of suitable lactones where these are desired, or other appropriate analyses familiar to the chemist.

Where stratification has not been employed, the mineral oil present is carried along in the mix to the subsequent step. Where stratification results and is taken advantage of for any reason, the aqueous soap layer is withdrawn and diluted. In this case any oil present would be in a separate layer, and if it is desired may be recovered in any manner, for example, by naphtha extraction especially where it is desired to recover and use the unsaponifiable oxidized oil.

After the acid treatment of the diluted soap solution, the undecomposed sodium soaps and any water-soluble organic acids or lactones which may have been set free remain in solution in the lower aqueous layer. The freed acids, float on top of the aqueous layer with the non-saponifiable oil present in the oxidized mass treated. If sufficient oil is not present, a small amount such as an equal volume of oil or other solvent for the liberated acids may be added to dilute the mass and assist stratification. The temperature for these operations ordinarily would be somewhat elevated for example 150° F. to 200° F. The layer of acids or acid-oil solution is removed and acid and/or water-washed one or more times, the wash liquor being settled and withdrawn after each wash. When mineral lubricating oil is added a naphthenic-type Western or California mineral lubricating oil is preferred especially where it is to be used later in preparing lubricants such as Diesel engine lubricating oil. This oil is employed for convenience in future handling of the acids.

The oil layer contains the oil-soluble weak acids, lactones and lactides, and is now drawn off and is ready for further use or treatment. If soaps of these materials are sought the oil-solution may be treated accordingly. This may be done by direct saponification by commingling with a suitable alkaline solution or by double decomposition especially where soaps of certain metals are required. Commingling with sodium hydroxide solution or other alkali metal hydroxide at suitable time will yield corresponding alkali metal soaps. Or, having obtained a sodium or potassium soap, a water solution of a salt of other desired metal may be added and the soap of the latter metal, e. g., Fe, obtained therefrom by metathesis. In some cases such other soaps may be obtained also by direct reaction with heat, as with the alkaline earth metals. In the case of calcium in particular, calcium hydroxide or hydrated lime in the form of a slurry may be commingled with the oil-acid solution at elevated temperatures such as between about 175° F. and 225° F. with agitation for two or three hours or until the desired saponification is obtained. The batch is then dehydrated with heat, as at 300° F. to 325° F. and settled, filtered or centrifuged while hot to remove excess alkali and by-products of saponification. The soaps are largely soluble in the oil, and the product is a concentrate of the calcium soap in oil, to which more oil may be added to yield any desired soap content. If further clarification is desired, this may be accomplished sometimes by stirring into the mixture a small quantity of an inert clay or other filter aid before filtration and while still hot.

In general, when organic acids are mentioned herein the term is intended also to include lactones and lactides which are the more stable non-acidic forms of the corresponding hydroxy acids formed in oxidation of petroleum fractions. When the stronger acids remaining in the form of water-soluble soaps in the original aqueous body are desired, they may be recovered by evaporating most of the water, cracking out the acids with dilute sulfuric acid or other mineral acid to decompose or neutralize the soaps, collecting the water-insoluble acids (if present), and fractionally distilling off the water and then the desired water-soluble organic acids, leaving behind sodium sulfate and the like. Such acids may in turn be saponified or salted out or used as such, as may be desired. They will be stronger acids, as measured by their ability to form salts in aqueous solution, than the water-insoluble, oil-soluble weaker acids previously recovered, and will, at least in general, be of lower molecular weight, except as the high molecular weight acids may be affected by excessive hydroxyl groups or the like.

This fractionation procedure may be carried on to effect separation of a greater number of fractions of the acids or acidic materials from the soaps upon the basis of varying acid strengths. This may be done by adding only sufficient mineral acid to the saponification batch with alkali metal hydroxide which contains the soaps in water-soluble form, to "crack out" that proportion of weakest acidic materials desired, recovering them from the surface as in solution in the oil layer; adding more acid to "crack out" the cut of next weakest acidic materials desired, while preferably adding also an additional amount of solvent oil as a carrier to receive the liberated oil-soluble materials, and recovering such layer of acidic materials; and repeating the operation to whatever extent desired until all the oil-soluble or water-insoluble acidic materials are recovered.

Oil-soluble soaps, such as calcium soaps or other alkaline earth metal soaps, may then be made by saponifying the various oil-acid solutions.

By such procedures, oil-soluble lactones and lactides could be recovered first by cracking the soaps of the weakest or lactone- and lactide-forming acids and recovering the lactones and lactides in the oil layer. Then the next weakest acids, and then stronger and stronger oil-soluble acids. The acidic, water-soluble materials likewise may be largely dehydrated and fractionated from the water solution of their soaps by cracking and fractionally distilling as above indicated to obtain as many cuts as desired; or selective solvent extraction may be employed to effect the separation of certain acids from others, as with ether.

In separating the oil-soluble materials, while the separation is along lines of relative acid strengths, there is in general also a separation as between higher and lower molecular weights be-

cause in general the higher molecular weight materials are apparently less acidic.

Again, where materials of weaker and stronger acidic character but approximately the same molecular weight are present in mixtures, a separation may be made because the weaker will "crack out" first, the soaps or salts of the stronger being in this sense more stable. Whereas, as between materials of similar strengths, a separation may be made along lines of selective solubility in various solvents; for example, the higher molecular weight materials being taken up in solution in oil or the like and the lower molecular weight materials passing into water solution as the salt where the whole batch is agitated to permit the selective solvent action to take place.

Thus, the invention is applicable to segregation of a great variety of oil-soluble organic acidic materials by "cracking out" the weaker acids first from their salts or soaps, while the stronger acids await the addition of further quantities of the strong mineral acid.

The invention may be applied to segregation of acids from coconut oil and the like, where high and low molecular weight acids are present and are desired to be separated as such or as soaps of the respective types of acids.

The invention is particularly applicable where it is desired to obtain soaps of high molecular weight relatively weaker acids, especially those weaker acids having more than about 10, 12 or 14 carbon atoms per molecule, which acids and their soaps are soluble in mineral lubricating oils for lubrication purposes. For example, calcium and other oil-soluble metal soaps, particularly the alkaline earth metal soaps, of these weaker organic acids, are useful in mineral lubricating oils, particularly the Western or naphthenic base oils above mentioned for use in severe service internal combustion engines. Here, from about 0.5% to 2% or 3%, or about 1% to 1.5% of these soaps produce oils generally having less tendency toward development of corrosive conditions in engines than oils containing other types of soaps, and also reduce tendencies toward valve and ring sticking and deposit of resinous and varnish-like materials on the engine parts.

It will be understood by those skilled in the art that the illustrative matter here given is not to be considered as necessarily limiting of the generic invention but merely as pointing out certain embodiments thereof.

We claim:

1. A process for the separation of soaps and acids thereof comprising forming water-soluble soaps of a mixture of stronger acids and of oil-soluble weaker organic acids and forming an aqueous solution of said soaps, supplying a quantity of mineral oil, adding to said soap solution an aqueous solution of a strong mineral acid to break the soaps of the portion of oil-soluble weaker organic acids desired, causing the released acids to rise with the oil and dissolve in said mineral oil to form a layer of acids in oil, and recovering said layer.

2. A method according to claim 1 wherein the oil is lubricating oil.

3. A method according to claim 1 and the additional step of converting the acids into oil-soluble soaps soluble in said mineral oil.

4. A method according to claim 1 wherein the mineral oil is lubricating oil, and the additional step of converting said acids into oil-soluble soaps in the presence of said oil, which soaps are soluble in said lubricating oil.

5. A method of separating organic saponifiable acids and their soaps comprising saponifying a mixture of stronger organic acids and weaker organic acids in a diluent in which the soaps are soluble and said weaker acids are insoluble, adding a strong mineral acid solution to decompose the soaps of a desired proportion of said weaker acids and liberate such proportion of acids, supplying mineral oil to act as a carrier for the liberated acids which are soluble in said mineral oil, collecting said liberated acids together with said mineral oil in a separate layer and removing them.

6. A method of separating organic saponifiable acids and their soaps comprising saponifying a mixture of stronger organic acids and weaker organic acids in a diluent in which the soaps are soluble and said weaker acids are insoluble, supplying mineral oil to act as a receiver for the liberated acids, said liberated acids being soluble in mineral lubricating oil, adding a strong mineral acid solution to decompose the soaps of a desired proportion of said weaker acids and liberate such proportion of acids, and then making further additions of mineral oil and mineral acid to liberate successive proportions of the oil-soluble acids, and separately recovering the oil-acid layers.

7. A method comprising producing a solution of soaps of a mixture of stronger and weaker organic acids in a solvent for said soaps, said weaker acids being soluble in mineral oil and insoluble in said solvent, acidifying the batch with mineral acid sufficiently only to liberate from their soaps a desired proportion of the weaker acids, collecting said liberated acids as a separate layer, supplying lubricating oil thereto and saponifying the acids to form oil-soluble soaps in said lubricating oil to yield a lubricant.

8. A method comprising oxidizing a highly paraffinic mineral oil fraction to yield stronger acids and oil-soluble weaker acids, saponifying said acids and effecting a solution of the soaps in a diluent in which the weaker acids are insoluble, adding mineral acid to liberate only oil-soluble, weaker acids, supplying oil as a carrier for said oil-soluble acids, and saponifying the oil solution of said weaker acids to yield oil-soluble soaps thereof in solution in the oil as a lubricant stock.

9. A method comprising producing a solution of soaps of a mixture of stronger organic acids and weaker organic acids in a solvent for said soaps, said weaker acids being soluble in mineral lubricating oil and insoluble in said solvent, acidifying the batch to liberate only those weaker organic acids desired, collecting said liberated acids, and forming oil-soluble soaps of said collected liberated acids and dissolving them in mineral lubricating oil.

10. A method according to claim 9 wherein mineral lubricating oil is present to dissolve said liberated acids and such acids are saponified in the presence of said oil.

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