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MANUFACTURE OF POLYVALENT METAL SOAPS

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This invention relates to the manufacture of polyvalent metal soaps, and more particularly polyvalent metal naphthenates from naphthenic acids such as are obtained from petroleum.

One of the principal objects of this invention is to provide a method of manufacturing metallic soaps of this character which is effective to secure a substantially increased yield of improved product in a simple and economical manner.

Other objects and advantages of the invention will be apparent from the following description and the accompanying claims.

In the manufacture of soaps, such as metallic naphthenates of this character, it has heretofore been the practice to effect double decomposition by the addition to a water solution of an alkali metal naphthenate of a water solution of a polyvalent or heavy metal salt to secure a precipitation of the polyvalent or heavy metal naphthenate with concomitant production of a salt of the alkali metal which remains in solution. In the copending application of Charles C. Towne, Serial No. 180,557, there is disclosed that greatly increased yields may be obtained by adding the polyvalent or heavy metal salt in solid form to the water solution of alkali metal naphthenate, thereby preventing secondary or side reactions which are found to occur when the polyvalent or heavy metal salt is added in solution form. Thereafter, a water-immiscible solvent in which the polyvalent or heavy metal naphthenate is soluble, such as benzol or naphtha, is added to dissolve the precipitated naphthenate; and the mix is allowed to stratify into a water layer and a solvent layer which are then separated.

In accordance with the present invention, further improvement in the manufacture of metallic soaps such as naphthenates of this character is effected by adding the water-immiscible organic solvent to the water solution of the alkali metal naphthenate, and then emulsifying this mix, prior to the addition of the polyvalent or heavy metal salt in solid form. Preferably the pH value of the emulsion is adjusted slightly on the alkaline side by the addition of a small excess of NaOH or other base, prior to the addition of the solid salt. By reason of the emulsification of the alkali metal naphthenate solution by the water-immiscible solvent, forming an oil in water emulsion, a better reaction of the added solid salt is obtained. Moreover, the proportion of water to naphthenic acids may be reduced, very satisfactory results being obtained by the use of from 2–3 parts of water to one part of naphthenic acids. The addition of the solid salt with precipitation of the polyvalent or heavy metal naphthenate in the immediate presence of the droplets of water-immiscible solvent causes the precipitated naphthenate to be taken up rapidly in solution in this solvent, thereby removing it from the zone of reaction and at the same time breaking the emulsion. In this manner, side reactions are avoided and an increased yield of desired product obtained.

The broken emulsion is then allowed to stratify into a water layer and a solvent layer containing the dissolved polyvalent metal naphthenate, and these layers are separated. Thereafter, the separated solvent layer is preferably washed with water one or more times to remove water soluble salts, and the washed solvent layer may then be mixed with a quantity of a heavy mineral oil fraction boiling above the boiling range of the solvent, such as a mineral lubricating oil, and this product is then filtered through an inactive clay to clarify the same. Following this filtration, the solvent is stripped off leaving a concentrate of the polyvalent metal naphthenate in the lubricating oil as a final product. This is particularly desirable where the product is to be used as an additive to a mineral lubricating oil.

Where the polyvalent metal naphthenate is desired to be obtained in solid form, the addition of the heavy petroleum fraction is omitted, and the solvent layer after washing and filtration is stripped directly.

The present invention is applicable to the manufacture of soaps of such metals as tin, iron, zinc, nickel, chromium, manganese, aluminum, copper, lead, and the like. For purposes of easy description, the expression "polyvalent metal" is hereinafter used throughout the description and claims to designate metals of this character. The present invention appears particularly applicable to the manufacture of such polyvalent metal soaps in which the metal exists in the "ous" form, such for example as stannous, ferrous, cuprous and the like.

Unusually good results have been secured by this method in the manufacture of stannous naphthenate, which is hereinafter described as a preferred embodiment of the invention. As an example, 1000# of purified naphthenic acids having a saponification value of 129 and a neutralization number of 125 were mixed with approximately 2440# of water in a steam heated agitator. The mix was heated to about 150–180° F., and then approximately 190# of a 49% NaOH solution was added with continued stirring. The quantity of caustic soda was calculated to neu-

tralize the naphthenic acids and form a substantially neutral solution of sodium naphthenate, there being a slight excess of NaOH to provide approximately 0.02% free NaOH. After agitation for a period of several hours to complete the neutralization, approximately 275 gallons of a sulfur-free narrow cut naphtha fraction was added together with an additional 42 gallons of water (approximately 336#), and the agitation continued at a temperature of 125–150° F. until a homogeneous oil-in-water emulsion was produced, the sodium naphthenate serving as an emulsifying agent. To this emulsion with continued agitation at a temperature of around 175° F. were added crystals of stannous chloride over a period of approximately ½ hour until 280# of crystals had been introduced. After agitation for a further period of approximately an hour, stirring was then stopped and the mix allowed to stratify into a lower water layer containing dissolved water soluble salts, and an upper naphtha layer containing dissolved stannous naphthenate. The water layer was then withdrawn, and the solvent layer washed twice by the addition of five barrels (42 gallons each) of water with stratification and separation of the water layer after each washing step, to thereby remove any water soluble salts remaining in the solvent layer.

To the washed solvent layer was then added 175#. of a distillate lubricating oil having a Saybolt viscosity of about 300 at 100° F., and the mix stirred at approximately 150° F. until a uniform solution was obtained. This mix was then filtered through an inert clay, such as Dicalite or filter cel on a Kelly Press, using approximately 100# of the clay to coat the leaves of the press, in order to clarify the solution of any suspended impurities. The solution was then stripped in a still with steam at 400° F. to remove the naphtha solvent, thereby obtaining 1031# of a concentrated lubricating oil solution of stannous naphthenate of a dark red color having a green cast and a neutralization number of 73.7. This concentrate contained approximately 888# of stannous naphthenate, representing a conversion of 96%. In other runs in accordance with this invention, conversions of as high as 98.5% have been obtained.

While an elevated temperature of the order of about 175° F. was employed in the above example during the precipitation of stannous soap, good results can be obtained by precipitation of the soap at temperatures varying from normal atmospheric temperatures up to said elevated temperature or higher. It is desirable to maintain temperatures, particularly the temperatures of stripping to remove the naphtha, as low as possible in order to preserve the desirable properties and color of the product. For this purpose, a low boiling cutter is employed so that it can be stripped at a comparatively low temperature, particularly with the aid of steam or vacuum or both.

While the invention has been particularly described above in connection with the manufacture of polyvalent metal naphthenates, it is to be understood that this invention is also applicable to the manufacture of polyvalent metal soaps of other acids, such as the higher fatty acids, including stearic, oleic, palmitic, etc., and mixtures thereof, and also the substituted fatty acids such as the halogenated fatty acids and the like.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. In the manufacture of a polyvalent metal soap from a water solution of an alkali metal soap, the steps which comprise emulsifying the water solution of alkali metal soap with a low boiling water-immiscible organic solvent, and adding a polyvalent metal salt, which tends to decompose in water, in solid form, unmixed with water, to the emulsion to cause a precipitation of polyvalent metal soap which passes into solution in the solvent and breaks the emulsion.

2. The method in the manufacture of a polyvalent metal naphthenate which comprises neutralizing naphthenic acids with a water solution of an alkali metal base to form a water solution of alkali metal naphthenate, then adding to the solution a low boiling water-immiscible organic solvent in which the polyvalent metal naphthenate is soluble and emulsifying the same, thereafter adding a polyvalent metal salt, which exists in the "ous" form and tends to decompose in water, in solid form unmixed with water to the emulsion to cause a precipitation of polyvalent metal naphthenate which passes into solution in the solvent and breaks the emulsion, and separating the polyvalent metal naphthenate from the resultant mix.

3. The method of claim 2 in which the polyvalent metal naphthenate is separated by allowing the broken emulsion to stratify into a water layer containing dissolved water soluble salts and a solvent layer containing dissolved polyvalent metal naphthenate, separating the layers, washing the separated solvent layer to remove remaining water soluble salts, adding a heavy petroleum oil to the washed solvent layer, filtering the resulting solution to clarify the same, and then removing the solvent by stripping to obtain a concentrate of the polyvalent metal napthenate in the heavy petroleum oil.

4. The method in the manufacture of stannous naphthenate which comprises neutralizing naphthenic acids with a water solution of an alkali metal base to form a water solution of alkali metal naphthenate, adding to the solution a low boiling water-immiscible organic solvent in which stannous naphthenate is soluble and forming a solvent-in-water emulsion thereof, then adding a stannous salt in solid form unmixed with water to the emulsion to cause precipitation of stannous naphthenate which passes into solution in the solvent, and separating the stannous naphthenate from the resulting mix.

5. The method of claim 4, in which the water-immiscible organic solvent is a naphtha fraction, and in which the stannous naphthenate is separated by allowing the broken emulsion to stratify and separate into a water layer containing dissolved water soluble salts and a naphtha layer containing dissolved stannous naphthenate, separating the layers, washing the separated naphtha layer to remove remaining water soluble salts, adding a mineral lubricating oil to the washed naphtha layer, filtering the resulting solution to remove suspended impurities, and removing the naphtha by stripping to obtain a lubricating oil concentrate of stannous naphthenate.

6. In the manufacture of a polyvalent metal naphthenate from a water solution of an alkali metal naphthenate, the steps which comprise

emulsifying the water solution with a low boiling water-immiscible organic solvent, and adding a polyvalent metal salt, which tends to decompose in water, in solid form, unmixed with water, to the emulsion to cause a precipitation of polyvalent metal naphthenate which passes into solution in the solvent and breaks the emulsion.

7. In the manufacture of stannous naphthenate from a water solution of an alkali metal naphthenate, the steps which comprise emulsifying the water solution with a low boiling water-immiscible solvent to form a solvent-in-water emulsion, and then adding a stannous salt in solid form unmixed with water to the emulsion to cause a precipitation of stannous naphthenate which passes into solution in the solvent and breaks the emulsion.

8. The method of claim 7 in which the pH value of the emulsion is adjusted to a slight alkalinity prior to the addition of the stannous salt.

9. The method in the manufacture of stannous naphthenate which comprises mixing 2–3 parts of water with one part of naphthenic acids, neutralizing with a water solution of an alkali metal base to form a water solution of alkali metal naphthenate using a slight excess of the base to adjust the pH value of the resulting water solution of alkali metal naphthenate to a slight alkalinity, adding to the solution a low boiling water-immiscible organic solvent selected from the group consisting of naphtha and benzol and agitating to form a solvent-in-water emulsion, then adding slowly to the emulsion with continued agitation crystals of a stannous salt unmixed with water to cause precipitation of stannous naphthenate which passes into solution in the solvent and breaks the emulsion, and separating the resultant solvent solution of the stannous naphthenate from the remaining water solution.

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