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PREPARATION OF METALLIC SOAPS

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This invention relates to manufacture of metal-organic compounds by direct reaction between a carboxylic acid and the metal in the metallic state.

Prior to my invention it was known that such reactions would occur simply by bringing together the acid and the metal but the reactions did not go to completion and the rate was too slow for practical results. The ordinary means for speeding up reactions did not accelerate the reactions to a sufficient degree. U. S. Patents 2,395,307 and 2,397,767 proposed to speed up the reaction by blowing the reaction mixture with air presumably to form oxide at the surface of the metal which would easily react with the acid. This was found to be unsuitable for the production of siccatives and allied products inasmuch as the product was dark and sludged badly, evidently due to the formation of oxidation products.

I have now discovered that certain metals in the metallic state can be reacted at a satisfactory rate and to a satisfactory degree of completion with organic acids by carrying out the reaction in the presence of an organic, monohydric alcohol having from 1 to 10 carbon atoms in the molecule, suitably a lower aliphatic alcohol or fenchyl or furfuryl alcohol or such an alcohol plus a lower aliphatic acid or a mixture thereof. An important advantage of this discovery is that no water is added nor formed during the reaction and accordingly, no drying is necessary.

The metals referred to are manganese, magnesium and calcium.

The organic acids referred to are aliphatic and alicyclic organic acids having from 8 to 22 carbon atoms in the molecule. The mono-carboxylic acids are preferred. The specific commercial materials which we consider most suitable for our process are: naphthenic acid; the higher fatty acids having from 8 to 22 carbon atoms in the molecule such as stearic acid, palmitic acid, oleic acid, and 2-ethyl hexoic acid. The list may also include tall oil, tall oil acids, rosin, rosin acids, and other commercial mixtures of acids such as those derived from fish oil, corn oil, coconut oil, linseed oil, castor oil, and cottonseed oil. These mixtures are made up entirely or nearly so of acids having from 8 to 22 carbon atoms.

The lower aliphatic acids referred to are formic, acetic, chloroacetic, propionic, chloropropionic, oxalic, citric, and tartaric acids.

The alcohols referred to are organic, non-aromatic, monohydric alcohols having not more than ten carbon atoms, e. g. lower aliphatic alcohols such as methanol, ethanol, isopropanol, and non-

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aromatic, cyclic, monohydric alcohols such as furfuryl alcohol and fenchyl alcohol.

In the practice of the invention the metal in the form of powder, granules, wire, shavings or the like is brought into contact with (1) the high molecular weight organic acid or a mixture of such high molecular weight acids and (2) a small proportion of a low molecular weight aliphatic alcohol or preferably a mixture of the low molecular weight alcohol and the low molecular weight acid. The weights of the metal and the high molecular weight acid may be calculated to stoichiometric proportions or there may be an excess of the metal or a small excess of the acid. The low molecular weight acid may be employed in catalytic proportions, e. g. from $\frac{1}{2}$ to 5% based upon the weight of the high molecular weight acid. The alcohol may be present to the extent of from $\frac{1}{2}$ to 5% of the weight of the high molecular weight acid and if both catalytic acid and alcohol are used, they may be present, taken together, to the extent of from $\frac{1}{2}$ to 10% of the weight of the high molecular weight acid. Oxidizing gases are not only unnecessary but are actually objectionable. Inert or reducing gases may be employed either by bubbling the same through the reaction mixture or using such gases to replace the air in the reaction vessel.

The metal may be in excess of the molecular equivalent of the high molecular weight acid by any amount since the excess at the end of the reaction may be filtered off. If the metal is in a finely divided state which gives faster reaction and is, therefore, desirable, the excess need not be great; but in order to get a high reaction rate in the case where the metal is not finely divided, a greater excess is used. In the case of 200 mesh metal in excess of $\frac{1}{4}$ mol of metal per mol of high molecular weight acid is satisfactory from the standpoint of reaction rate.

The temperature of the reaction may be suitably from 100° C. to 160° C. but preferably should be from 135° to 140° C.

In some cases the reaction carried out in the presence of an excess of metal results in a basic compound. This may be desirable but if it is not, the basic compound may be treated with additional calculated quantities of siccativ acid to give a neutral product.

The following specific examples will serve to illustrate the invention:

Example I

To 200 grams of naphthenic acid of acid value 244 were added 24 grams of manganese metal in

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the form of 100 mesh powder, 5 grams of methanol, 5 grams glacial acetic acid and 135 grams of mineral spirits. The mixture was refluxed at a temperature of 135-140° C. for a period of 3 hours after which the excess manganese metal was filtered off. The result was a mineral spirits solution of manganese naphthenate having a metal content of 5.93%, an acid value of 22.5 and total solids at 105° C., 60.2%.

Example II

An otherwise similar run to Example I was made, substituting isopropanol for methanol. It gave comparable results.

Example III

An otherwise similar run to Example I was made, substituting tall oil for the naphthenic acid. A very good reaction was completed in two hours and fifteen minutes giving a basic product in a mineral spirits solution.

Example IV

To 200 grams of 2-ethyl hexoic acid were added 38½ grams of manganese metal in the form of 100 mesh powder, to ½ gram fenchyl alcohol, 2½ grams acetic acid and 325 grams of mineral spirits. This mixture was refluxed at a temperature of 135-140° C. for 6¾ hours after which the excess manganese was filtered off. The result was a mineral spirits solution of manganese ethyl hexoate having a metal content of 6.22%, an acid value of +13.3, a total solids content of 43.3%, and a color of 14 on the Gardner Scale.

Example V

To 200 grams of linseed fatty acids were added 12 grams of calcium metal turnings, 2½ grams methanol, 2½ grams acetic acid, 20 grams cello-solve as a viscosity reducer and 165 grams of mineral spirits. The mixture was refluxed for six hours and filtered to remove any excess metal, giving a solution having 2.9% calcium, an acid value of +19.4 and a total solids content of 57%.

Example VI

To 200 grams of tall oil were added 9 grams of magnesium metal, 5 grams of methyl alcohol, 5 grams glacial acetic acid, and 125 grams of mineral spirits. The mixture was refluxed for six hours at 135-140° C. after which the excess magnesium was filtered off giving a solution containing 2.35% Mg, and having an acid value of -0.5 and a total solids content of 68.6%.

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Example VII

An otherwise similar run to Example IV, substituting furfuryl alcohol for fenchyl alcohol gave comparable results to Example IV.

Having thus described my invention, what I claim is:

1. In the manufacture of compounds of metals of the class consisting of manganese, magnesium and calcium, the steps of reacting together in the temperature range from approximately 100° C. to approximately 160° C. the metal in metallic state and a high molecular weight, organic, mono-carboxylic acid of the class consisting of aliphatic, alicyclic, rosin and tall oil acids having from 8 to 22 carbon atoms in the molecule, the metal being present in excess of the amount required to react with said acid and the reaction being carried out in the presence of cooperating catalysts, one thereof essentially consisting of from ½% to 5% by weight of an aliphatic alcohol having from 1 to 10 carbon atoms in the molecule, and the other thereof essentially consisting of from ½% to 5% of a low molecular weight organic acid of the class consisting of formic, acetic, propionic, chloro-propionic, oxalic, citric and tartaric acids, percentage being based on the weight of said high molecular weight organic acid.

2. A process according to claim 1 wherein said metal is manganese and said mono-carboxylic acid is naphthenic acid.

3. A process according to claim 1 wherein said metal is manganese and said mono-carboxylic acid is 2-ethyl hexoic acid.

4. A process according to claim 1 wherein said metal is manganese and said mono-carboxylic acid is tall oil acid.

5. A process according to claim 1 wherein said metal is manganese and said mono-carboxylic acid is naphthenic acid.

6. A process according to claim 1 wherein said metal is calcium and said mono-carboxylic acid is naphthenic acid.

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