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METHOD OF PREPARING HYDROXY HEAVY METAL SOAP COMPOSITIONS

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This invention relates to a method of preparing mixtures of hydroxy metal soaps in vehicles and while capable of use in the production of soaps of various metals, is especially useful in the preparation of hydroxy copper naphthenates alone or in combination with other metallic soaps including normal copper naphthenates. Thus it is possible to obtain, for example, hydroxy copper naphthenate soaps of practically any desired hydroxy content.

In my previous Patent No. 2,116,321, dated May 3, 1938, I described the preparation of hydroxy metal soaps including hydroxy copper naphthenate in such manner that the end product was generally in dry pulverulent form. This required, in the course of the incorporation of such hydroxy metal soaps into other compositions, mechanical grinding or other steps, so as to bring about proper dispersion of the hydroxy soap in the associated composition. This procedure is attendant with certain difficulties. It is well known that grinding of pulverulent matter is a laborious and relatively expensive operation and often requires special apparatus including dust collecting apparatus, etc. Furthermore, the production of the hydroxy metal soaps in pulverulent form requires drying equipment of relatively large floor area and the drying operation usually requires a protracted time cycle. Following the drying, the hydroxy metal soap has to be comminuted by such means as grinders, sifters, etc. in order to yield a substantially uniform pulverulent material. In addition to these drawbacks, it is also necessary to select the raw material components carefully, so that the resultant composition is non-sticky, and will not tend to agglomerate. Moreover it is necessary that water remaining from the double decomposition reaction be substantially removed in order to permit the proper functioning of the end product. This has been accomplished by mechanical drying.

I have found that all of the above mentioned disadvantages accruing to the production and use of pulverulent hydroxy metal soaps, may be substantially eliminated through the employment of the present invention next to be described.

In carrying out the present invention in its preferred practical form, I employ three solutions A, B and C: Solution A representing an aqueous solution of an alkali soap of a predetermined organic water-insoluble acid, together with free and unreacted alkali hydroxide, and Solution B representing an aqeous solution of the water-soluble salt of the selected heavy metal. When these two solutions are brought together under agitation, there is formed the hydroxy metal soap of such metal and acid. This hydroxy metal soap precipitates out in the form of a water-insoluble magma. It is separated from the by-product salts and a large portion of the water by mechanical means, such as filter pressing. The magma may also receive subsequent water washings to free it entirely from the by-product salts.

It is also within the purview of this invention to eliminate at this stage of the method the removal of any of the water and/or the said by-product salts.

Following this the magma is then mixed under agitation with Solution C which is preferably wholly or in part volatile. Ordinarily it is preferred to employ for this purpose a vehicle including a volatile solvent because this aids in the subsequent removal of water.

The vehicle employed may be selected from a broad range. For example, I have found it very satisfactory to employ as a vehicle a petroleum solvent, known under the trade name "Sovasol." Likewise, I have satisfactorily employed coal tar hydrocarbons, e. g., xylol.

The solvent may be selected from the broad class of organic substantially water-insoluble liquids which are employed in the arts, generally, as solvents, such as paint solvents, rubber solvents, etc. They are not necessarily a solvent for the hydroxy metal soaps forming part of the magma to which I have referred.

The mixture of the hydroxy metal soap magma in said vehicle is thereupon subjected to the action of heat to effect a dehydration operation. This may be carried out at atmospheric pressure or in vacuo, and I have found that under these conditions, the water present in the hydroxy metal soap magma will distill off readily and completely, leaving behind the hydroxy metal soap in finely dispersed form in the vehicle.

It is necessary during the dehydration operation that there is continually present a part or all of the vehicle associated with the hydroxy metal soap so that, as the operation proceeds, the soap becomes thoroughly dispersed throughout the vehicle. Aside from this critical factor, the actual amount of vehicle employed may vary within wide limits depending upon conditions. It has been found expedient in some cases to return continuously to the reaction apparatus those portions of the volatile vehicle which distill off with the water, so as to maintain within the reaction kettle substantially uniform conditions.

The material produced at the conclusion of

the dehydration or drying step may contain different amounts of vehicle, so as to be in the form of a relatively thick paste or in the form of a pourable liquid, depending upon what is desired for particlar uses, or if it comes from this operation in the form of a thick paste, it may be diluted with further amounts of the vehicle as it may be desired. In any event, the degree of dispersion attained by the procedure of this invention is superior to that which may be obtained by mechanically dispersing the pulverulent hydroxy metal soap in the same vehicle.

I have referred to the production of a soap of a single metal during double decomposition steps described. I may, however, if so desired effect double decomposition of a plurality of metals at the same time or, if desired, I may carry out double decomposition as described for one metal and also the same steps in connection with one or more additional metals, and thereafter commingle or bring together the resulting magma of the several metals before jointly dehydrating them in the drying step which I have described.

I have also referred to the use of a water-insoluble organic acid, in the production of the hydroxy metal soap according to this invention. I do not limit this invention to the use of a single acid alone, but may employ a plurality of such acids for this purpose. The acids employed are, however, substantially water-insoluble and substantially non-volatile and should be such as to form the water-insoluble hydroxy metal soaps. They can be aromatic acids, such as para-chlorbenzoic acid, aliphatic acids, such as oleic acid, linseed oil fatty acids, and cyclic acids, such as naphthenic acid. Tall oil may also be used for this purpose.

The formation of the hydroxy metal soap in form of its water magma has been described as the initial process step of this invention. It is possible, however, to precipitate first either a hydroxy metal soap of greater basicity than is desired in the dehydrated product or it is also feasible to precipitate the straight hydroxide of the metal. In these cases, it is possible to include in the vehicle employed in drying, a sufficient amount of the organic acid to react with the metal hydroxide or hydroxy metal soap of the metal present, so as to bring about the desired hydroxy content of the dehydrated product.

The production of a wide variety of metal soaps may be accomplished by the method of this invention according to the metals which enter into the reaction. For example, I may use such metals as copper, zinc, lead, cobalt, manganese, iron and generally the other heavy metals which are capable of forming water-insoluble hydroxides.

For the purpose of concrete example, I shall now describe the production of a hydroxy copper naphthenate soap useful for various purposes, but more particularly as a fungicidal and insecticidal agent. This compound may also form a component part of orchard sprays for pest control.

EXAMPLE 1

Solution A

	Pounds
Water	1,200
Aqueous solution of caustic soda of 25% strength	233
Naphthenic acid (acid No. 210)	129

Solution B

	Pounds
Copper sulphate crystals (25% copper)	190
Water	700

Solutions A and B were commingled under agitation. The hydroxy copper naphthenate which was formed precipitated out in the form of a water-insoluble magma. The entire reaction mixture was then filter pressed to remove the larger portion of the water. The hydroxy metal soap magma remaining in the filter press was washed to remove the by-product salts. The hydroxy metal soap magma containing approximately 70% water was then incorporated under agitation into the following vehicle which may be referred to as:

Solution C

	Pounds
Sovasol (a volatile petroleum distillate solvent manufactured by The Standard Oil Co. of New York)	200

The mixture of Solution C with the hydroxy metal naphthenate magma was heated under agitation in a closed kettle to a temperature of approximately 100° C. The water was thus distilled off together with a portion of the volatile petroleum distillate solvent, a part of which solvent upon condensation was fed back into the kettle.

The foregoing example contained 259 lbs. less naphthenic acid than the normal compound would require. On a percentage basis, it contained 33% of the amount required to form the normal compound.

The dehydration of the hydroxy metal naphthenate soap during this dehydration step was so complete that upon completion, there was present less than 1% of water in the end product. The end product, in the approximate amount of 264 lbs., constituted a mobile mixture of the hydroxy metal naphthenate in the vehicle. The consistency was that of a heavy, but flowable liquid. The concentration of the hydroxy metal soap was 70% (metal content approximately 18%), the balance being the petroleum distillate solvent.

It was particularly notable that in the end product, the resulting mixture of the metallic soap was practically of colloidal fineness in dispersed form—in fact, much finer and complete than could possibly be obtained by mechanical means. This is an important factor because, generally speaking, the efficiency of many compositions, particularly fungicides, depends upon very fine state of dispersion.

It is to be noted that the end product is a true hydroxy copper naphthenate because it has been formed through the double decomposition of copper sulphate with the combination of alkali naphthenate soap and free alkali hydroxide. More specifically, in the reaction referred to, there was present approximately 140 pounds of free and unreacted aqueous sodium hydroxide solution of 25% strength, or more than 50% of the total amount of sodium hydroxide introduced into the reaction.

The reaction carried out in the example just given was at atmospheric pressure, although, if desired, it may be carried out in vacuo.

In the example given, all of the acid which entered into the reaction was incorporated in Solution A. I have found it possible, however, and in some cases desirable, to incorporate part

of the acid to be employed in Solution A and the remainder in Solution C, the condition being in every case that the total amount of organic acid employed is insufficient to form the normal compound and therefore perforce the hydroxy compound must be formed. As exemplary of the latter procedure, note the following:

EXAMPLE 2

Solution A

	Pounds
Water	1,200
Aqueous solution of caustic soda of 25% strength	233
Naphthenic acid (acid No. 210)	50

Solution B

	Pounds
Copper sulphate crystals (25% copper)	190
Water	700

Solution C

	Pounds
"Sovasol"	200
Naphthenic acid (acid No. 210)	79

The foregoing example contained 259 lbs. less naphthenic acid than the normal compound would require. On a percentage basis, it contained 33% of the amount required to form the normal compound.

Yield of the composition: approximately 264 lbs. of dispersion paste, containing 70% total solids—18% copper.

The advantage of the procedure of this example is that the physical bulking of the hydroxy metal soap magma in the filter press is reduced by the omission of part of the organic acid and this means that a smaller bulk including less water need be handled in the filter presses.

The naphthenic acid which forms part of Solution C reacts completely through the dehydration cycle, so that the end product, namely, the hydroxy copper naphthenate, is identical in composition with the copper hydroxy naphthenate of Example 1 wherein the total amount of naphthenic acid was present during the magma formation.

EXAMPLE 3

Solution A

	Pounds
Water	1,000
50% aqueous solution of caustic soda	97
Oleic acid (acid No. 195)	120

Solution B

	Pounds
Copper sulphate crystals (25% copper)	159
Water	600

Solution C

	Pounds
Xylol	400
Linseed oil	100

In the process of dehydration, sufficient xylol is removed with the water distilling off to yield 265 lbs. of a paste composition containing approximately 64% of the hydroxy soap—15% copper.

The composition represents a dispersion of hydroxy copper oleate in a mixed vehicle.

The formula contains 228 pounds oleic acid less than the normal compound would require and on a percentage basis, it contains approximately 34% of the amount required to form the normal type.

EXAMPLE 4

Solution A

	Pounds
Water	1,200
Aqueous solution 25% of caustic soda	233
Tall oil (acid No. 160)	200

Solution B

	Pounds
Copper acetate (32% copper)	153
Water	800

Solution C

	Pounds
"Solvesso" #3 (a petroleum solvent)	300

In the dehydrating process sufficient "Solvesso" is removed to yield 408 lbs. of a composition containing approximately 63% of the hydroxy copper soap—12% copper.

The composition represents a dispersion of hydroxy copper tallate in a volatile solvent vehicle.

The formula contains 309 lbs. less tall oil than the normal compound would require. On a percentage basis it contains approximately 39% of the amount required to form the normal copper-tallate soap.

EXAMPLE 5

Solution A

	Pounds
Water	900
Flake caustic soda (76% Na_2O)	60
Tall oil	250
Anti-oxidant (alpha-naphthol)	3
(The anti-oxidant being dissolved in the tall oil)	

Solution B

	Pounds
Copper sulphate (25% copper)	189
Water	1,200

Solution C

	Pounds
Naphthenic acid (acid No. 230)	50
Mineral spirits	400

After the dehydrating process, the weight of the composition is adjusted to 470 lbs. The composition then contains approximately 76% hydroxy copper soap—10% copper. The product represents a dispersion of a mixed hydroxy copper tallate-naphthenate soap, in a volatile vehicle. The formula contains only 61% of the amount of tall oil—naphthenic acid required to form the normal copper soap.

EXAMPLE 6

Solution A

	Pounds
Water	2,000
25% aqueous solution of caustic soda	350

Solution B

	Pounds
Water	1,500
Copper sulfate (25% copper)	285

Solution C

	Pounds
Petrolatum	350
Naphthenic acid (acid No. 220)	200

After the process of dehydration, the weight of the composition is adjusted to 460 lbs. This composition which is in paste form represents a dispersion of hydroxy copper naphthenate in a non-volatile vehicle. The metal content of this paste is approximately 15%. This formula con-

tains only 36% of the amount of acid which would be required to form the normal copper soap.

EXAMPLE 7

1000 lbs. of a hydroxy copper naphthenate dispersion paste, prepared as described in Example 1, are commingled with:

2000 lbs. of a mineral spirits solution of normal copper naphthenate, such solution carrying 9% copper content.

There is thus obtained 3000 lbs. of a composition representing a combination of a hydroxy copper soap with a normal copper soap—the total copper content of this formula being approximately 12%.

EXAMPLE 8

500 lbs. of a hydroxy copper soap, obtained as described in Example 2, is commingled with:

50 lbs. of normal mercury compound of 20% mercury content.

This process yields 550 lbs. of a composition representing a combination of a hydroxy copper soap with a normal mercury compound.

EXAMPLE 9

Solution A

	Pounds
Water	1,000
50% aqueous solution potassium hydroxide	120
Para-chlor benzoic acid	110

Solution B

	Pounds
Copper sulfate (25% copper)	100
Zinc sulfate (23% zinc)	43
Water	500

Solution C

	Pounds
Xylol	300
Neutral rosin oil	50

In the process of dehydrating, sufficient xylol is removed with the water to yield 250 lbs. of end product. This represents a mobile dispersion of a mixed copper-zinc hydroxy soap in a vehicle. The metal contents are approximately:

	Percent
Copper	10
Zinc	4

This formula contains only 64% of the acid which would be required to form the normal soaps.

EXAMPLE 10

Solution A

	Pounds
Flake caustic soda	89
Water	1,100
Naphthenic acid (acid No. 240)	220
Hydrogenated rosin (acid No. 160)	10

Solution B

	Pounds
Lead acetate (54% lead)	428
Water	1,200

Solution C

	Pounds
High flash naphtha	400

The weight of the end product obtained after dehydration is adjusted to 770 lbs. This composition represents a dispersion of hydroxy lead soap of two acids in a volatile vehicle. The metal content of this formula is approximately 30% lead. The formula contains only 43% of the full amount of acid which would be required to form the normal soap.

EXAMPLE 11

Solution A

	Pounds
Water	800
25% aqueous solution of caustic soda	250
Oleic acid (acid No. 195)	200

Solution B

	Pounds
Water	1,200
Lead acetate (54% lead)	300

Solution C

	Pounds
Mineral spirits	500
Petroleum resin	75

After the process of dehydrating, the weight of the resultant end product is adjusted to 650 lbs. The composition represents a dispersion of hydroxy lead oleate in a vehicle. The lead content of the formula is 25%. This formula contains only 45% of the full amount of acid required to produce the normal lead soap.

EXAMPLE 12

Solution A

	Pounds
Water	200
Caustic soda	57
Naphthenic acid (acid No. 230)	160

Solution B

	Pounds
Cobalt sulfate crystals (20% cobalt)	212
Water	300

Solution C

	Pounds
Mineral spirits	400
Neutral rosin oil	200

After dehydration, the weight of the end product is adjusted to 645 lbs. The composition represents a dispersion of hydroxy cobalt naphthenate in a vehicle. The metal content is approximately 5%. This formula contains 53% less acid than the normal cobalt naphthenate would require.

EXAMPLE 13

Solution A

	Pounds
Water	900
10% aqueous solution of caustic soda	830
Tall oil (acid No. 160)	150
2-ethylhexoic acid (acid No. 400)	100

Solution B

	Pounds
Iron sulfate (20% iron)	211
Water	600

Solution C

	Pounds
Xylol	500

After the dehydration process, the weight of the resultant end product is adjusted to 525 lbs. This composition represents a dispersion of hydroxy iron soap in a volatile vehicle. The metal content is 8%. This formula carries only 55% of the full amount of acids required to form the normal iron soap.

EXAMPLE 14

Solution A

	Pounds
Water	600
Potassium hydroxide	30
Naphthenic acid (acid No. 270)	170
Alpha naphthol anti-oxidant	2

(The anti-oxidant being dissolved in the acid)

Solution B

	Pounds
Manganese sulfate (20% manganese)	390
Water	1,400

Solution C

	Pounds
Benzoic acid	30
Xylol	400

The weight of the end product, after dehydration is adjusted to 780 lbs. This composition represents a mixture of hydroxy manganese naphthenate-benzoate in a volatile vehicle. The metal content is 10%. This formula contains only 75% of the full amount of acids required to obtain the normal manganese soap.

EXAMPLE 15

Solution A

	Pounds
Water	1,200
Aqueous solution of caustic soda, 25% concentration	233

Solution B

	Pounds
Copper sulfate crystals	190
Water	700

Solutions A and B were commingled under agitation. The copper hydroxide which was formed precipitated out in the form of a water-insoluble magma. This was then commingled with Solution C which comprises:

	Pounds
"Sovosol"	200
Naphthenic acid (acid No. 210)	129

The weight of the end product after dehydrating was adjusted to approximately 264 pounds. The end product represents a dispersion of hydroxy copper naphthenate in a volatile vehicle. The formula contains 70% of the hydroxy copper naphthenate—18% copper. The composition carries only 33% of the amount of naphthenic acid which would be required to form the normal compound.

The various hydroxy soaps to which I have referred may be used for a wide variety of purposes. For example, and without limitation, they may be employed as fungicides, as active ingredients in anti-fouling ship bottom paints, as insecticides, as mildewproofing agents, as catalytic agents, as paint and varnish driers, ink driers, linoleum composition driers, as agent to prevent loss of drying on ageing of paints and other coating compositions, as wetting agents, etc.

The metal soaps produced, as hereinbefore described, may be used as the sole metallic soap constituent of other compositions as stated, or may be used in combination with other metallic soaps in such compositions. For example, as a fungicide it may be desirable to employ a combination of normal copper naphthenate and my hydroxy copper naphthenate. It is possible for this purpose to mix together copper hydroxy soap dispersion, produced as hereinbefore described, with a normal copper soap either in the same or in different quantities as may be desired. Such a mixture may then be further associated with other ingredients to form, for example, a treating medium for the fungicidal-water-proofing and flame-proofing treatment of textiles.

Another combination which has been found to be of considerable utility comprises a mixture of the hydroxy lead naphthenate dispersion of this invention with other metallic naphthenates prepared by conventional methods, e. g., it may be desirable to incorporate into a coating composition, such as a paint, a plurality of metal soaps which may include my hydroxy lead naphthenate dispersion and cobalt naphthenate and manganese naphthenate made by conventional methods.

Having thus fully described the invention, what I claim as new and desire to secure by Letters Patent is:

1. Process of producing a dispersed hydroxy heavy metal soap in a dehydrated organic vehicle, which comprises: thermally dehydrating in a substantially water immiscible organic vehicle an aqueous magma comprising the reaction product of an alkali soap of at least one substantially water-insoluble non-volatile organic acid, free alkali hydroxide and a sufficient quantity of water-soluble salt of at least one heavy metal to completely react with the alkali soap and the free alkali hydroxide, whereby said hydroxy heavy metal soap is finally dispersed in substantially insoluble form in said dehydrated organic vehicle.

2. Process of producing a dispersed hydroxy heavy metal soap in a dehydrated organic vehicle, which comprises: thermally dehydrating in a substantially water immiscible organic vehicle an aqueous magma comprising the reaction product of an alkali hydroxide and a sufficient quantity of at least one water-soluble heavy metal salt to completely react with the alkali hydroxide, there being present in said vehicle during said dehydration step a quantity of at least one substantially water-insoluble non-volatile organic acid in an amount insufficient to produce the normal salt of such heavy metal but sufficient to produce hydroxy metal soap, whereby said hydroxy heavy metal soap is finally dispersed in substantially insoluble form in said dehydrated organic vehicle.

3. Process of producing a dispersed hydroxy copper soap in a dehydrated organic vehicle, which comprises: thermally dehydrating in a substantially water immiscible organic vehicle an aqueous magma comprising the reaction product of an alkali soap of at least one substantially water-insoluble non-volatile organic acid, free alkali hydroxide and a sufficient quantity of a water-soluble copper salt to completely react with the alkali soap and the free alkali hydroxide, whereby said hydroxy copper soap is finally dispersed in substantially insoluble form in said dehydrated organic vehicle.

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