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ART OF INCORPORATING DRYING METALS
IN PAINTS, VARNISHES, LINOLEUMS, INKS,
ETC.

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This invention relates to driers for paints, varnishes, enamels, linoleums, printing inks, etc., and the invention is directed, more particularly, to the incorporation of drying metals into such end products of commerce.

Drying metals, as contemplated by this invention, include, among others, the following: lead, cobalt, iron, manganese, nickel, zinc, calcium, barium, cerium.

It has been heretofore common to incorporate salts of these drying metals in paints, varnishes, linoleums, etc., in certain well defined ways. For example, these salts have been introduced in powdered form, by grinding them with vehicles at room temperature. They have also been associated with vehicles by commingling them in liquid form. It has also been the practice in some instances to fuse metal compounds, including the desired drying metal or metals, with the vehicles into which they are to be incorporated, such, for example, as by cooking litharge with rosin or cobalt acetate with a linoleum vehicle.

In the preparation of cooked driers, it has been customary to employ a vehicle which may consist of oils or resins, or both, in conjunction with some volatile solvent which is added after the reaction is completed. The metal compounds previously employed for this purpose have been of a wide variety. For example, cooked lead driers have been commonly produced from litharge, lead acetate, and also from the solid naphthenate, resinate or linoleate of lead. In the case of manganese, the raw material has commonly been manganese dioxide, manganese borate, manganese acetate, as well as the solid resinate, naphthenate or linoleate of manganese. In the case of these solid compositions, they have been derived by fusion or by double decomposition. Cobalt has been produced from cobalt carbonate, cobalt acetate, or the solid linoleate, resinate or naphthenate of cobalt.

The employment of all of these metal compounds in the process of cooking presents certain well recognized difficulties. For example, when using manganese dioxide, it is very difficult to obtain complete reaction. With litharge, or lead acetate, the lead tends to settle to the bottom thereby interfering with the heating, as well as making it still more difficult to bring it into solution in the total mass. In the case of the acetates, such as cobalt acetate, it is practically impossible to completely drive off the acetic acid and any remnants of this acid which remain will seriously interfere with the stability and drying efficiency of the drier. In the use of solid driers,

such as naphthenates or linoleates, they are usually tough and dense masses which are difficult to manipulate. The resinates have poor solubility and require long periods of the application of heat in order to dissolve them in the vehicle. All of these difficulties which have attended conventional prior practice are satisfactorily overcome by the present invention in a simple, economical and efficient way as will be hereinafter more fully described.

The present invention deals primarily with the incorporation of appropriate, substantially water-insoluble, organic hydroxy salts of the drying metals into the compositions into which they are to be introduced, at such elevated temperatures as to bring about chemical reaction between the hydroxy metal salt and the vehicle, whereby the hydroxy metal salt is solubilized and thus enters solution in such vehicle. Under prior practice, where elevated temperatures were used with metal compounds, such as cobalt acetate or litharge, or manganese borate, such hydroxy metal salts have not heretofore been used.

By "solubilized," I mean that the drying metal salt is rendered soluble in the vehicle into which it is to be incorporated whereby it is enabled to go into solution therewith as specified.

In practically carrying out the present invention, the hydroxy metal salt or salts employed are first prepared. The following procedures have been found to give highly satisfactory results.

COMPOSITION A.—Hydroxy cobalt salt (23%
cobalt metal content)

Ingredients:	Pounds
Caustic soda.....	100
Naphthenic acid (acid No. 240).....	225
Water	2800
Cobalt sulphate crystals.....	331
Water	400

PROCEDURE

Introduce into a tank, equipped with an agitator, the 2800 lbs. water. Then add the caustic soda and then the naphthenic acid. Thoroughly mix and, while agitation continues, add the cobalt sulphate solution prepared by dissolving the cobalt sulphate crystals in the 400 lbs. of water. When the action is completed, decant the salt solution, filter and dry.

The resulting product is a dry, loose, relatively porous hydroxy cobalt salt of blue color. It may be broken down into nuggets or fine or coarse particle sizes as may be desired.

Total yield—278 lbs.

COMPOSITION B.—Hydroxy manganese salt (24% manganese metal content)

Ingredients:	Pounds
Caustic soda	101.5
Naphthenic acid (acid number 240) ..	212
Water	2000
Manganese sulphate (30% man- ganese)	240
Water	600

PROCEDURE

Same as with Composition A: i. e., prepare aqueous-caustic soda-naphthenic acid-solution and add thereto aqueous manganese sulphate solution, and thereafter decant, filter and dry.

The resulting product is a dry, loose, relatively porous, hydroxy manganese salt which may be broken down as hereinbefore stated.

Total yield—280 lbs.

COMPOSITION C.—Hydroxy iron salt (28% iron metal content)

Ingredients:	Pounds
Caustic soda	93
Naphthenic acid (acid number 234) ..	185
Water	2500
Ferric chloride crystals	300
Water	400

The procedure and sequence of operation is as described in connection with Composition A.

Total yield—220 lbs. of hydroxy iron salt.

COMPOSITION D.—Hydroxy lead salt (64% lead metal content)

Ingredients:	Pounds
Caustic soda	155
Naphthenic acid	216
Water	1500
Lead acetate	720
Water	900

The procedure and sequence of operation is as described under Composition A.

Total yield—630 lbs. of hydroxy lead salt.

It is also possible to vary the formula and metal content of the hydroxy metal salts employed. E. g., a cobalt of from 18% to 28% has been prepared by following the procedure of Composition A, but with variation in the relative percentages of the reactants.

It is also possible to use other acids than naphthenic acid, as well as mixtures of acids for the preparation of the compounds. The criterion of the suitability of any acid or mixture of acids is:

1. Pulverulency of finished product.
2. Reactivity of finished product in cooking.
3. Solubility and stability of finished product in the vehicle.
4. Color, odor, etc.
5. Substantially water-insolubility of end product hydroxy salt.

COMPOSITION E.—Hydroxy lead salt (62% metal content)

Ingredients:	Pounds
Hydrogenated rosin	40
Naphthenic acid (acid number 265) ..	200
Caustic soda	155
Water	1300
Lead acetate	720
Water	900

PROCEDURE

It is convenient to heat the hydrogenated rosin to 250° F. and then mix it with the naphthenic acid. Process is then as described with reference to Composition A.

Total yield—670 pounds of hydroxy lead salt.

COMPOSITION F.—Hydroxy manganese salt (30% metal content)

Ingredients:	Pounds
2-Ethylhexoic acid	95
Oleic acid	83
Caustic soda	101½
Water	2000
Manganese sulphate (30% man- ganese)	240
Water	600

Sequence and process same as hereinbefore described.

Total yield—240 lbs. of hydroxy manganese salt.

COMPOSITION G.—Hydroxy cobalt salt (20% metal content)

Ingredients:	Pounds
Castor oil fatty acid	230
Caustic soda	91
Water	2800
Cobalt sulphate crystals	300
Water	300

Process as previously described.

Total yield—307 lbs. of hydroxy cobalt salt.

I have found that compositions of the character hereinbefore described, may be utilized for the production of commercial end products, such as cooked driers, paints, varnishes, linoleums, printing inks, and other coating compositions, having vehicles which are organic, water-insoluble and film-forming and which depend upon oxidation for drying.

In order that the present invention may be clearly understood with reference to the cooking of driers into vehicles, I shall compare prior practice with that of the present invention, by first giving a conventional formula and then the corresponding procedure of this invention.

EXAMPLE Ia.—Lead-manganese Japan drier (conventional practice)

Raw linseed oil	gallons ..	2½
East India gum	pounds ..	72
Litharge	do	16
Red lead	do	15½
Black oxide of manganese	do	22½
Solvent	gallons ..	90

Total yield—95 gals.

This drier requires about 2 hours of cooking in the varnish kettle and a considerable sludge is formed due to the limited solubility of the inorganic metal salts used.

EXAMPLE I.—This invention

In the formula of Example Ia, I substituted, for the litharge, red lead and oxide of manganese, the following:

	Pounds
My hydroxy lead salt of 64% metal content ..	30
My hydroxy manganese salt of 24% metal content ..	35

and found that the processing time was cut in half; that the yield was increased by 5 gals. to 100 gals.; and that the drier possessed a drying

strength at least equal to the drier of Example Ia. Furthermore, it had a paler color, was free from sludge and its solubility was greater than the end product of Example Ia. I thus not only obtained a better end product drier but accomplished marked economies in its preparation because the cooking time was cut in half. Moreover, there was a pronounced absence of that frothing which accompanied the procedure of Example Ia, and, consequently, larger batches may be prepared in the same capacity kettle. With the present invention, the reaction is much faster and vigorous agitation (such as is necessary when using litharge or other inorganic salts) is not here required.

EXAMPLE IIa.—Conventional practice

Rosin	-----pounds	750
Lime (calcium hydroxide)	-----do	250
Perilla oil	-----gallons	30
Litharge	-----pounds	48
Manganese borate	-----do	38
Solvent	-----gallons	177

Total yield—208 gals.

This formula requires about 1½ hours processing. The resultant drier will show a considerable amount of suspended material and will be dark in color.

EXAMPLE II.—This invention

By substituting my hydroxy lead and manganese salts for the inorganic lead and manganese compounds by employing:

	Pounds
Hydroxy lead salt, 64% metal	48
Hydroxy manganese salt, 24% metal	27

the time of processing was reduced by 38%. The total yield of the end product was increased by 8 gals., making a total of 216 gals. The drying performance of this formula was slightly superior to that of Example IIa, although its yield was increased. Its color was definitely better and its stability in vehicles was far superior to that of the formula for which it was substituted.

EXAMPLE IIIa.—Conventional practice

Rosin	-----pounds	200
Linseed oil	-----gallons	15
Lime (calcium hydroxide)	-----pounds	14
Cobalt acetate	-----do	12
Thinner	-----gallons	80

Total yield—110 gals.

Due to the very pronounced foaming and frothing of the cobalt acetate, it was necessary to introduce this salt in small portions. Furthermore, it required considerable time and attention to boil off all acetic acid which was liberated in the course of the reaction. The overall time of reaction with this formula was approximately 3 hours.

EXAMPLE III.—This invention

When an equal amount of my hydroxy cobalt salt (23% metal content) was substituted for the cobalt acetate of Example IIIa, it was found that the entire reaction could be carried out in one hour. The hydroxy cobalt salt reacted with very little foaming and became soluble practically instantaneously. Furthermore, the yield in this case was increased by approximately 2 gals. to a total of 112 gals. The stability of this formula was definitely greater than of the cobalt acetate drier. Furthermore, its solubility in ve-

hicles was much better than that of Example IIIa. Its color was also superior to that of the latter formula. In spite of the increased yield obtained, the drying performance was slightly superior to that of Example IIIa. This perhaps might be due in some degree to the fact that often driers prepared from cobalt acetate retain some acetic acid, which exerts a detrimental effect upon drying.

EXAMPLE IVa.—Conventional practice

Rosin	-----pounds	400
Linseed oil	-----gallons	30
Linseed oil fatty acids	-----do	5
Litharge	-----pounds	40
Cobalt acetate	-----do	20
Thinner	-----gallons	160

Total yield—230 gals.

As in Example IIIa, the introduction of cobalt acetate was accompanied by strong foaming. It was necessary to stir vigorously and the entire reaction was rather slow, requiring about 3½ hours to complete. The end product carried some suspended matter due to the fact that it is impossible to obtain complete conversion of the inorganic salts employed in this formula.

EXAMPLE IV.—This invention

When in place of the cobalt acetate and litharge, 18 lbs. of my hydroxy cobalt salt (23% metal) and 45 lbs. of my hydroxy lead salt (64% metal) were employed, the entire reaction was carried out in 1½ hours. The total yield increased by 5 gals., making a total of 235 gals. The resultant drier was perfectly clear and had superior drying performance to the end product of Example IVa. Its staining was less and its color was far better than that of the cobalt acetate drier. Its solubility and stability in paint and varnish vehicles was very much superior to that of the acetate drier. Furthermore, due to the complete absence of acetic acid in this formula, there was no danger of discoloring sensitive lake colors in enamels, etc. in which it might be incorporated. On the contrary, acetate driers often, due to the retention of acetic acid, exert a highly objectionable reaction and discoloration on certain sensitive pigments which are employed in the manufacture of paints and enamels.

EXAMPLE Va.—Conventional practice

	Pounds
Improved linseed oil	620
Rosin	400
Fumed litharge	80
Manganese dioxide	15
Cobalt hydroxide	5
Mineral spirits	1800

Total yield—2600 lbs.

This formula requires 3¼ hours for processing. The resultant drier carried some suspended matter due to incomplete reaction of the inorganic metal compounds used. The color was rather dark and the staining power objectionably high.

EXAMPLE V.—This invention

When a substitution with my hydroxy metal salts is made by employing

	Pounds
Hydroxy lead salt (64% metal)	100
Hydroxy manganese salt (24% metal)	20
Hydroxy cobalt salt (23% metal)	12

it was found that the entire process could be accomplished in 1¼ hours. The total yield increased by not less than 200 lbs. due to the presence of the hydroxy salts themselves, and also due to the much lower cooking loss because of faster reaction and lower temperatures. In spite of the extra yield, the resultant drier showed a slightly superior drying performance over the end product of Example Va. Its color and staining were much more satisfactory than of the drier which it replaced. Furthermore, its solubility and stability in vehicles in which it was incorporated was much better than that of Example Va.

It is also possible to utilize the hydroxy metal salts hereinbefore described in the preparation of solid driers, such as, for example, resinate driers, with the absence of any oils or solvents. For example, cobalt resinate or cobalt linoleate is often prepared by fusion of cobalt acetate with rosin or linseed oil fatty acids. For this purpose, it is possible to substitute the hydroxy cobalt salt (23% metal) for the acetate.

I have also found that it is possible to react my hydroxy metal salts with various other water-insoluble, organic acids at temperatures above the decomposition temperatures of such salts. Examples of such acids are oleic acid, ricinoleic acid and capric acid. While these acids, as such, are not necessarily film-forming, their metal salts may be used in film-forming vehicles.

EXAMPLE VIA.—Conventional practice

228.6 lbs. of rosin were fused, and 21.4 lbs. of cobalt acetate (23% metal) were then added. Very strong frothing and foaming resulted, which necessitated feeding the acetate in very small portions. The total time of reaction was approximately 3 hours. It was also necessary to boil off as much of the acetic acid which was liberated in the process, as possible, because even small amounts of retained free acetic acid have an adverse effect upon the drying performance of the cobalt resinate.

EXAMPLE VI.—This invention

When in place of the cobalt acetate an equal amount of my hydroxy cobalt salt (23% metal) was used (21.4 lbs.), the reaction proceeded very speedily and with very little foaming. The entire process was carried out in less than 1 hour. The resultant product showed superior color, drying performance and stability, to the acetate drier.

It was also found possible to produce similarly the resinates or linoleates of the hydroxy lead or manganese salts.

EXAMPLE VIIA.—Convention practice

43 lbs. of manganese acetate were introduced into a batch of 207 lbs. of linseed oil fatty acids. Due to the strong foaming which always accompanies the fusion of acetates, and due to the necessity of driving off as much as possible of the liberated acetic acid, it was required to react for a period of about 2¼ hours.

EXAMPLE VII.—This invention

When in place of the manganese acetate the equivalent amount of my hydroxy manganese salt was used in the fusion, the entire reaction progressed so rapidly and with so little foaming that it was concluded in less than 1 hour. The end product possessed better stability and superior drying performance to the acetate drier.

I also found that it is possible to utilize my hydroxy metal salts by cooking them directly into oils, varnishes, etc. For various reasons, such as gasproofing, quicker bodying, better drying, higher gloss, etc., drying metal salts, such as litharge, cobalt acetate, lead acetate, as well as the solid naphthenates, resinates or linoleates are sometimes directly introduced into the oil, varnish or other vehicle while being heated. For this purpose my hydroxy compounds work out excellently.

EXAMPLE VIIIA.—Conventional practice

In a 100 gal. batch of heavy bodied quick drying varnish

	Pounds
Litharge.....	0.5
Manganese borate.....	0.2

were employed during cooking of the varnish.

EXAMPLE VIII.—This invention

It was found that the use of 0.6 pound of my hydroxy lead salt (60% metal content) and 0.1 pound of my hydroxy manganese salt (30% metal content) would produce better drying, better color and freedom from sludging.

From the foregoing examples, it will appear that in carrying out the present invention in its preferred form, I first produce an aqueous solution of an alkali salt of an organic acid capable of rendering the substantially water-insoluble hydroxy salt of at least one predetermined drying metal soluble in a film-forming vehicle at a temperature above the reaction point of such hydroxy salt. This solution also contains free hydroxide of such alkali metal. I separately produce an aqueous solution of a water-soluble, inorganic salt of such drying metal in excess of the amount to molecularly react with the normal alkali salt of said acid for reacting with the caustic alkali of the first solution. I then commingle these solutions so that they may interact to produce a substantially water-insoluble organic hydroxy salt of the drying metal or metals employed. At the conclusion of the reaction, I isolate the hydroxy metal salt thus produced, preferably dry the same and in appropriately divided form introduce it into an organic, water-insoluble, film-forming, oxidizable vehicle and raise the temperature to a point sufficient to react my hydroxy drying metal salt with said vehicle to produce the desired end product.

It will be noted from the foregoing examples that the use of my hydroxy drying metal salts, as specified, has many important advantages, for example:

1. They are very easy to handle. (They may be either in powder form or in the form of nuggets or even coarser particles if desired.)

2. They react very rapidly and with a minimum of foaming.

3. They permit the cooking of larger batches because of quick reaction and the absence of foaming.

4. They introduce no extraneous compounds or acids into the cooked drier which might ultimately exert a detrimental effect upon drying performance.

5. They do not introduce into the drier any extraneous acids such as acetic acid, which might react and discolor certain paint and enamel pigments.

6. They disperse and dissolve so rapidly in the kettle that strenuous agitation is unnecessary.

7. They do not form a sediment in the kettle

during the reaction, such as is usually the case with customary metal salts.

8. Because they disperse and dissolve so quickly in the cooking vehicle they do not reduce to the metal and thus become inactive and worthless such as is often the case when metal compounds, such as litharge, are used.

9. They react at relatively low temperatures which results in a reduction in cooking losses and fuel economies.

10. The end product driers are non-sludging and, therefore, do not require tanking for a protracted period, which is usually necessary with cooked driers because of the presence of sludge in them.

11. The resultant driers made from them are paler in color than similar driers made from materials such as manganese dioxide.

12. The end products possess improved solubility and stability in the usual paint and varnish vehicles.

13. They are non-hygroscopic and, therefore, retain their ease of handling even under humid conditions. This is most definitely not the case with certain inorganic salts such as cobalt acetate, which lumps together under humid conditions.

14. They are water-insoluble.

The examples hereinbefore given are illustrative of the invention, but the same is to be commensurate with the appended claims.

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

1. The process of producing a solution of a hydroxy salt of a drying metal in an oxidizable film-forming material of the class consisting of drying oils and oil varnishes, which comprises producing an aqueous solution containing an alkali metal salt of a water insoluble non-volatile, non-aromatic organic acid capable of rendering the hydroxy salt of a predetermined drying metal soluble in said film-forming vehicle at a temperature above the reaction point of said hydroxy metal salt and said vehicle and also containing free hydroxide of the alkali metal, separately producing an aqueous solution of a water-soluble inorganic salt of said drying metal in sufficient quantity to react with the alkali salt of said acid and also the free hydroxide of said alkali metal, then mixing the said solutions to form a hydroxy metal salt of the drying metal, isolating the said hydroxy metal salt, adding a minor quantity of

said salt to such an oil or varnish material, and thereafter heating the mixture to a sufficiently high temperature to effect complete chemical reaction and solution between the said hydroxy salt and said oil or varnish material.

2. The process of producing a solution of a hydroxy salt of a drying metal in an oxidizable film-forming material of the class consisting of drying oils and oil varnishes, which comprises producing an aqueous solution containing an alkali metal salt of naphthenic acid and free hydroxide of the alkali metal, separately producing an aqueous solution of a water soluble inorganic salt of said drying metal in sufficient quantity to react with the alkali salt of the naphthenic acid and also the free hydroxide of said alkali metal, then mixing the said solutions to form a hydroxy naphthenate salt of the drying metal, isolating the said hydroxy naphthenate salt, adding a minor quantity of said salt to such an oil or varnish material, and thereafter heating the mixture to a sufficiently high temperature to effect complete chemical reaction and solution between the said hydroxy naphthenate salt and said oil or varnish material.

3. The process of producing a solution of a hydroxy salt of a drying metal in an oxidizable film-forming material of the class consisting of drying oils and oil varnishes, which comprises producing a hydroxy metal salt of a drying metal and a water insoluble, non-volatile, non-aromatic organic acid capable of rendering such hydroxy salt of such drying metal soluble in an oxidizable film-forming material of said class, then adding a minor quantity of said hydroxy drying metal salt to such an oil or varnish material, and thereafter heating the mixture to a sufficiently high temperature to effect complete chemical reaction and solution between said hydroxy salt and said oil or varnish material.

4. The process of producing a solution of a hydroxy naphthenate salt of a drying metal in an oxidizable film-forming material of the class consisting of drying oils and oil varnishes, which comprises producing a hydroxy naphthenate salt of a drying metal, then adding a minor quantity of the said hydroxy metal salt to such an oil or varnish material, and thereafter heating the mixture to a sufficiently high temperature to effect complete chemical reaction and solution between the said hydroxy salt and said oil or varnish materials.

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