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DRIER AND DRYING OIL COMPOSITION

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This invention relates to siccatives comprising the cobalt, manganese, lead and certain other polyvalent metal salts of alkylated phenol monocarboxylic acids and the combination thereof with drying oils.

When an unalkylated phenol carboxylic acid such as for example salicylic acid, is converted into its polyvalent metal salts, it is found that they are practically insoluble in aromatic, hydroaromatic, or aliphatic hydrocarbons and that they can only be incorporated as siccatives in drying oils by boiling them with the latter. This operation tends to discolor the oil and to decompose the salts partly into phenol and metal carbonate which reacts with the fatty acids present in the oil to form oil-soluble soaps. Such compositions dry poorly and discolor badly in white oil enamels. They also thicken up on standing, especially in the presence of certain pigments; and when thinned with varnish thinners tend to precipitate out the metal salts. The polyvalent metal salts of salicylic acid and its isomers (meta-, and para-hydroxy benzoic acids) are therefore inefficient siccatives.

I have made the discovery, that if one or more alkyl groups are present as a side chain in the aromatic nucleus of the phenol-carboxylic acid molecule, and especially if such alkyl groups contain more than two carbon atoms per group, that the polyvalent metal salts of such alkylated phenol-carboxylic acids are readily soluble in the cold in aromatic hydrocarbons such as benzene, toluene, xylene, etc., as well as in turpentine; and upon slight warming in naphtha, kerosene, gasoline and other organic solvents which are ordinarily used for thinning varnishes. Due to their high degree of solubility both in hydrocarbons and in fatty oils of the drying or semi-drying type at relatively low temperatures, and the ease with which they may be incorporated with paints, varnishes, printing inks, synthetic resins of the drying oil type (made from phthalic anhydride, polyhydric alcohols and drying oil fatty acids), oil enamels, and the like, and the accelerated drying which they impart to such compositions, without causing excess discoloration, precipitation, or skinning, these polyvalent metal salts of alkylated phenol carboxylic acids are very efficient siccatives for compositions containing drying oils.

The compounds which I have found to be especially suitable as siccatives for drying oil type of materials as described above, are the polyvalent metal salts, more especially the cobalt, manganese, and lead salts, of acids of the type comprising para-isopropyl salicylic acid, p-secondary butyl salicylic acid, normal amyl salicylic acid, secondary amyl salicylic acid, di- isopropyl salicylic acid, hexyl salicylic acid, heptyl salicylic acid, p-secondary octyl salicylic acid and the homologues or isomers thereof.

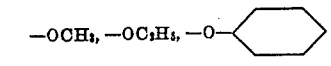
It is herein understood that this invention is not limited to the polyvalent metal salts of the alkylated salicylic acids above, but includes those of the alkylated meta- and p-hydroxy benzoic acids, as well as those of the ether derivatives of these alkylated phenol carboxylic acids in which the hydrogen atom of phenolic OH group is replaced by a hydrocarbon radicle, examples of such acids being the methoxy-, ethoxy-, or phenoxy-alkylated benzoic acids and their homologues.

The term "polyvalent metal" as referred to herein, is understood to include, not only the cobalt, manganese, and lead salts which are the most important siccatives, but also the vanadium, cerium, cadmium, thallium, nickel, tin, mercury, copper, iron, chromium, zinc, bismuth, aluminum, calcium, titanium, magnesium, and uranium salts which act as siccatives in varying degrees. The most active of the practical siccatives may be considered to be the cobalt, manganese and lead salts since small amounts of these compounds in the form of the alkylated phenol carboxylic acid salts (0.05% cobalt or manganese, or 0.20% lead calculated as metal on the weight of oil to be dried) accelerate the rate of drying of oils, paints, varnishes etc. markedly. The aluminum, calcium, magnesium, and zinc salts act as hardening agents in larger amounts (5–15% metal on the weight of the oil) and are herein included under the term "siccatives" even though their action is not entirely catalytic but also to a greater extent mechanical, behaving in this respect as resins. The mercury, copper, and bismuth salts have toxic properties in addition to siccative action and when present in larger amounts in oil varnishes and paints, act as efficient repellents of marine organisms, when applied in the form of paints or coatings on marine piling, ships' bottoms, and prevent mould and decay when applied to rope, hemp, textiles, wood, etc. They may also be used in salves as antiseptic ointments in conjunction with oily materials.

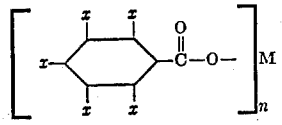
Furthermore these salts being readily soluble in butyl acetate, acetone, and other organic solvents such as are used in nitrocellulose lacquers or cellulose acetate lacquers may readily be incorporated as resins in such cellulosic composi-

tions and behave therein as lacquer gums promoting adhesion.

All of the polyvalent metal salts of the type herein described contain either a free phenolic OH group or an etherified phenolic group such as

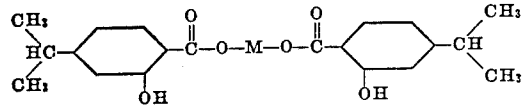


and the like; and only the hydrogen atom of the carboxyl group is replaced by the metal radical. In other words they have the general formula:

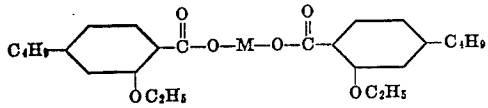


where "M" represents a polyvalent metal, "*n*" represents the number of effective valences of said polyvalent metal and wherein one "*x*" is a hydroxyl group or etherified hydroxyl group, any other "*x*" is an alkyl group, and the remaining *x*'s are hydrogen of the benzene nucleus.

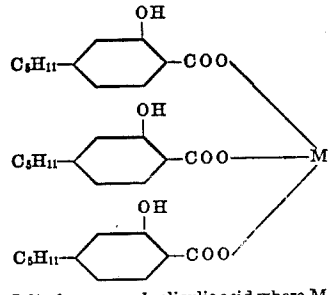
Examples of this formula which together with their isomers and homologues come within the scope of this invention are the following:



Salt of p-isopropyl salicylic acid where M is a divalent metal.



Salt of p-secondary butyl ethoxybenzoic acid where M is a divalent metal.



Salt of p-sec amyl salicylic acid where M is a trivalent metal.

it being understood as stated above that the phenolic OH group or the phenolic ether group need not necessarily be ortho to the carboxyl group, but may be in any other available nuclear position. The alkyl group also need not be para to the carboxyl but may be in any other available nuclear position. However, since the para-alkylated salicylic acids are the easiest and cheapest to prepare, I prefer the polyvalent metal salts thereof for the purposes of this invention, as illustrated by the formulas above.

I have found that if the phenolic hydrogen atom is replaced by the metal radicle that the resulting salts i. e. phenates are practically insoluble in varnish thinners and very unstable in drying oils, so that it is essential that the salts used be the so-called "mono-salts". These can be prepared by a method which leaves the phenolic hydrogen atom unreplaced by metal, as described later herein. If the phenolic hydrogen atom is etherified, of course this difficulty is eliminated as the metal can replace only the hydrogen atom of the carboxyl group.

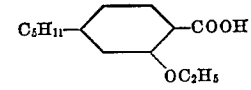
In order to more fully describe the general method by which the above salts may be prepared and used, the following examples are given.

Example 1

100 grams p-isopropyl salicylic acid is carefully neutralized with a 10 percent solution of sodium bicarbonate until the solution just changes brom-thymol blue indicator from yellow to a pale blue (pH7–7.6). The solution now contains the monosodium carboxylate having a free phenolic group. To this solution is added a slight excess of a 10% solution of a water-soluble, polyvalent metal salt, cobalt surfate, for example. A heavy blue precipitate of cobalt-para-isopropyl phenol carboxylate is obtained. This may be filtered off, washed, and dried, or it may be dissolved while still wet in an organic solvent such as toluene, or ethylene dichloride and the water separated therefrom, after which the salt is obtained by evaporating, or steaming off the solvent. A dark blue hard resinous mass is thus obtained which is dried in vacuo at about 80° C. When powdered, the cobalt salt thus obtained is readily soluble in esters, ketones, hydrocarbons, drying and semi-drying oils, oil varnishes, etc. It contains 14 to 14.5 percent by weight of metallic cobalt and is an efficient siccative. To dry oil compositions, mix into them sufficient of the salt to furnish a concentration of 0.05% cobalt upon the weight of the oil to be dried. This may readily be done by first dissolving the salt in varnish makers' naphtha or in turpentine and adding this solution to the oil composition. In the case of raw linseed oil which ordinarily requires about 24 hours to dry siccative, the drying time is cut to about 8 hours in the above case.

Example 2

100 grams of ortho-ethoxy-para-secondary amyl benzoic acid



is exactly neutralized with a sodium hydroxide solution using phenolphthalein as indicator and to the solution is added an excess of an aqueous solution of any polyvalent metal salt, for example manganous chloride. The heavy precipitate is filtered off, washed and dried. It is readily soluble in the solvents mentioned above and may be purified by dissolving in toluol, filtering, and recovering the residue by steam distilling off the solvent. The salt contains about 10% by weight of manganese. For a siccative, sufficient of it is dissolved in the drying oil composition to furnish 0.05% of manganese on the weight of the oil.

Example 3

100 grams of p-secondary octyl-salicylic acid is converted into its monosodium carboxylate as described above in Example 1, and the solution thereof treated with a slight excess of any water-soluble polyvalent metal salt, for example lead nitrate or lead acetate. The heavy white precipitate of lead salt is filtered off, washed, and dried in vacuo at 80° C. It is then dissolved in hot toluene, filtered from traces of insoluble matter and recovered from the filtrate by evaporating off the toluene. It forms a white powder which contains about 29% lead. For use in drying oil compositions, sufficient of the salt to furnish 0.25–0.50% lead upon the weight of the oil to be dried, is employed. This may be in-

corporated direct by gently heating the oil and sprinkling in the salt.

In a manner analogous to that described above, the other polyvalent metal salts of alkylated phenol carboxylic acid may be obtained and used. Mixtures of the cobalt and lead, or manganese and lead salts may be used as siccatives if desired. A typical varnish which dries satisfactorily has the following formula:

100 lbs. ester gum (or other suitable resin)
22 gallons China-wood oil
3 gallons linseed oil
275 lbs. V M & P naphtha
0.25 lbs. cobalt salt of p-isopropyl salicylic acid
0.60 lbs. lead salt of p-sec octyl calicylic acid

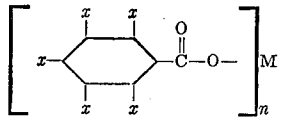
The two salts are dissolved separately in about 10 lbs. of the V M & P naphtha by warming to about 75° C. and the solution thus obtained added to the varnish.

It is understood that the salts may be incorporated with linseed oil, tung oil, and other drying oils or in coating, printing, or resin compositions prepared therefrom by any of the usual methods at present employed in the art. When incorporated properly they give drying oil compositions having qualities superior to those ordinarily obtained from the present well known varnish siccatives.

My co-pending patent application Serial No. 381,682 covers broadly the corresponding salts of alkylated benzoic acids and therefore I do not claim the latter compounds in this application.

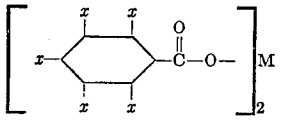
What I claim as new is:

1. A composition of matter comprising an auto-oxidizable varnish containing as a siccative a polyvalent metal salt of a nuclear alkylated phenol monocarboxylic acid derivative, said salt having the general formula



where "M" represents a polyvalent metal, "*n*" represents the number of effective valences of said polyvalent metal, and wherein one "*x*" is a member of the class consisting of hydroxy-, alkoxy-, and aryloxy-groups, another "*x*" is an alkyl group, and the remaining "*x*'s" are hydrogen.

2. A composition of matter comprising a drying oil varnish type of material containing a siccative which is a polyvalent metal salt of a nuclear alkylated phenol monocarboxylic acid derivative, said salt having the general formula



where "M" represents a member of the group consisting of cobalt, manganese, and lead, and wherein one "*x*" is a member of the class consisting of hydroxy-, alkoxy-, and aryloxy-groups, another "*x*" is an alkyl group, and the remaining "*x*'s" are hydrogen.

3. A composition of matter comprising an auto-oxidizable varnish containing as a siccative a polyvalent metal salt of a nuclear alkylated phenol monocarboxylic acid, said salt having the hydrogen atom of the phenolic hydroxy group unreplaced by a metal radical.

4. A composition of matter comprising an auto-oxidizable varnish containing as a siccative a polyvalent metal salt of a nuclear alkylated phenol carboxylic acid in which the phenolic hydrogen atom is replaced by a hydrocarbon radical.

5. A composition of matter of the kind described in claim 3, in which the polyvalent metal of the salt is a member of the group consisting of cobalt, manganese, and lead.

6. A composition of matter as set forth in claim 4, in which the polyvalent metal of the salt is a member of the group consisting of cobalt, manganese, and lead.

7. A composition of matter comprising an auto-oxidizable varnish containing as a siccative a polyvalent metal salt of a nuclear alkylated salicylic acid, said salt having the hydrogen atom of the phenolic hydroxyl group unreplaced by a metal radical.

8. A composition of matter comprising an auto-oxidizable varnish containing as a siccative a polyvalent metal salt of a nuclear alkylated salicylic acid ether.

9. A composition of matter comprising an auto-oxidizable varnish containing as a siccative a polyvalent metal salt of a salicylic acid having at least one nuclear hydrogen atom replaced by an alkyl group containing from 3 to 8 carbon atoms inclusive and having its phenolic hydroxyl group unreplaced by a metal.

10. A composition of matter as set forth in claim 9 in which the polyvalent metal of the salt is a member of the group consisting of cobalt, manganese, and lead.

11. A composition of matter comprising a drying oil type of varnish material containing as a siccative the mono-cobalt salt of para-isopropyl salicylic acid.

12. A composition of matter comprising a drying oil type of varnish material containing as a siccative the mono-cobalt salt of para-secondary butyl-salicylic acid.

13. A composition of matter comprising a drying oil type of varnish material containing as a siccative the mono-cobalt salt of para-secondary amyl-salicylic acid.

14. A composition of matter comprising a drying oil type of varnish material and a mono-cobalt salt of a nuclear alkylated salicylic acid in which the alkyl group contains more than 2 carbon atoms and is para to the phenolic OH group.

15. In the method of accelerating the drying of auto-oxidizable varnishes the step which comprises incorporating therewith as a siccative a polyvalent metal salt of the type set forth in claim 1.

16. In the method of accelerating the drying of auto-oxidizable varnishes the step which comprises incorporating therewith as a siccative a polyvalent metal salt of the type set forth in claim 2.

17. In the method of accelerating the drying of auto-oxidizable varnishes the step which comprises incorporating therewith as a siccative a salt of the type set forth in claim 14.

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