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ORGANIC DRIERS IN ORGANIC FILM FORMING COMPOSITIONS

Charles A. Coffey, Elmhurst, and Russell T. Ryan and Lynwood N. Whitehill, Chicago, Ill., assignors to The Sherwin-Williams Company, Cleveland, Ohio, a corporation of Ohio

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1

This invention relates to the employment of a novel class of compounds as replacements for the lead soaps normally used as drier catalysts in drying oil containing coating compositions.

Heretofore, the oil-soluble salts of a variety of organic acids have been the principal siccative materials used as catalyst to promote the "drying" of compositions containing unsaturated fatty acid groups. The three principal metal organic soaps employed are the lead, cobalt and manganese salts of high molecular weight organic compounds, e. g., rosinates, naphthenates and oilsolates or long chain fatty acid soaps. Other metals known to have some siccative effect include iron, zinc, calcium and nickel salts and soaps, but their use is more specific than the three principal metals named.

The three principal driers named are known to have an individual effect in drying oil fatty acid group containing coating compositions, and it is general practice to use the cobalt, lead and manganese salts or soaps in combination to avail of the individual stimulus to drying contributed by each metal present.

It is fairly generally agreed in the art as to theory that the metallic soaps function: (1) to shorten or eliminate the normal induction period preceeding the observable drying character of the unsaturated oils, (2) to accelerate the absorption of oxygen by the drying oil, (3) to cause gelation or solidification of the drying oil film at a lower total oxygen absorption than in the absence of the metal drier, and (4) to decrease the amount of oxygen absorption over the maximum absorption occurring in the absence of metal driers. Briefly stated, the drying of an oil film is believed to be initiated by oxidation and completed by polymerization within the film, and that both types of reaction are accelerated by the presence of metal driers.

The three principal metal driers are known to have many objectionable characteristics including high consistency at high metal content, tendency to sludge out and tendency to increase viscosity upon age after manufacture.

However, the lead driers have certain objectionable qualities which are of a more serious nature. One principal objection to lead driers is the toxic quality of lead itself.

During the last several decades, attention has been focused upon the toxic quality of lead in paints by numerous court actions involving lead poisoning. It has been alleged that children have become the victims of lead poisoning by chewing the paint off their cribs, and cattle by a

2

similar attack on fences and barns painted with lead-containing paints. As a result, many manufacturers of articles intended for use by children as in toys and furniture have insisted that such coatings be absolutely lead free. This was a difficult requirement as lead is considered almost essential to obtain "through-dry" necessary to quality finishes.

Another objection to lead driers has been the uncertainty of behavior of world markets in relation to its price and availability. Particularly during war periods, availability of lead for peacetime requirements becomes a serious problem.

Accordingly, we have directed our efforts toward purely organic compounds containing no metals at all which might be useful to supplant lead entirely.

As a result of a research project undertaken with this view as a goal, we have discovered that not only can lead soaps be eliminated by substitution therefor of a particular class of purely organic compounds, but in several instances actual improvements in siccative behavior over the usual lead soaps has been obtained. It has been further found that the substitutes for lead are more specific in their catalytic effect than is lead, and while all function as driers in a particular system, one of the group hereinafter disclosed may out-perform another. So far we have no full explanation for this phenomenon but we believe that it may be related to the molecular weight of the given organic drier. Our present research was conducted purely on a weight for weight substitution basis and it is reasonable to assume that slightly less amounts of some outstandingly useful compounds and slightly more of others in given formulations may result in greater economy in some cases and greater siccative quality in other applications, attention being given to molecular weights.

It is the broad object, therefore, to provide a drier catalyst for use in coating compositions containing drying oil fatty acid groups, said catalysts being purely organic in nature, having a similar behavior and function to metallic soaps presently employed as driers therein.

In general, this broad objective has been accomplished through the use of metal-free organic compounds containing from seven to eighteen carbon atoms and a carbonyl group, said compound selected from the class consisting of aliphatic aldehydes and substituted phenols wherein said substituent is characterized by the presence in said substituent of a carbonyl group.

The use of compounds other than the metal salts and soaps of higher molecular weight fatty acids has been priorly suggested. However, as far as the applicants are aware, the prior art has not been concerned with driers for unsaturated drying oil fatty acid containing coating compositions to an appreciable extent. Hexa-substituted ethanes have been suggested as possible driers, and certain mercaptans have been indicated as having an effect upon unsaturated maleic type resins. Cyanamide, acrylonitrile, guanyl urea compounds and lauro-guanamine have also been priorly suggested.

In making the tests and comparisons for the purpose of this research, tests were carried out in an air-conditioned room where temperature, humidity and light conditions were kept quite constant.

As it is usually customary to employ lead driers in conjunction with cobalt and manganese driers, the tests were further made upon the drying oil containing compositions having present from 0.025% to 0.30% cobalt, based on the metal and the vehicle solids, and in many cases an additional manganese salt present from 0.005% to 0.05% on the same basis of calculation.

An additional control test was carried through simultaneously containing only the metallic driers other than lead as a further means of comparison of drier activity of the nonmetallic organic compounds under test.

Comparative tests were conducted on identical vehicles, e. g., one aliquot portion of a selected vehicle would contain as an additive the conventional amount of the lead soap or drier and another aliquot portion of the same vehicle would carry an equivalent amount by weight to the lead soap of the purely organic compound under test.

The quantities of the purely organic compounds used in the tests ranged from 0.25% to 2.0% based on the total vehicle solids of the particular drying oil containing vehicle tested. The preferred range of percentage was found to be from 0.5% to 1.75% based on the said total vehicle solids content of the coating.

A series of eight different qualities of coating vehicles containing drying oil fatty acid groups were selected for the purpose of evaluation of the compounds tested. These vehicles contained from 100% drying oil in the outside house paint vehicle to as low as 52% of oil modification in one of the alkyds employed. Six of the vehicles selected are further described and identified in Table I.

A number of the compounds tested were objectionable from a practical viewpoint, though actually found to promote drying of paint films. In some instances, bad discoloration limits the application of the driers to darker colors and blacks. In other cases, odor of a persistent nature limits usage to outside application where odors are not confined. While skinning tendencies were observed with some vehicles and the purely organic driers, in general, by direct comparison we found an advantage in respect to non-skinning in favor of the purely organic driers herein disclosed.

Among the non-metal containing organic compounds tested and found useful as having a similar function to the lead soaps as driers in conjunction with the unsaturated fatty acid groups of oleoresinous varnishes are the following:

A. *Carbonyl compounds—Aliphatic aldehydes*

Octa-decenyl aldehyde
2-ethyl hexaldehyde
n-Decyl aldehyde
3,5,5-trimethyl hexaldehyde
Citronnellal
Cinnamic aldehyde

B. *Carbonyl compounds—Substituted phenolic nucleus*

p-Hydroxy benzaldehyde
Vanillin
Salicylaldehyde
p-Hydroxy propiophenone
β-Methyl umbelliferone
p-Anisaldehyde
2-hydroxy,3-methoxy benzaldehyde
2-hydroxy,5-chloro benzaldehyde
Piperonal
Benzaldehyde

An interesting result was observed in the comparison of certain of the aromatic ring compounds containing aldehydic substituents. Test results indicated that if the ring was substituted in the para position to the carbonyl containing group with a phenolic group, outstanding drier activity was obtained. When the hydroxy group was in a meta position the results were not unusually good, but when that group was ortho in position to the carbonyl containing group, improvement over the meta substituted compounds was observable. It was thus found that the first described substituents, e. g., a hydroxy group para to the carbonyl containing group gave preferred results with ortho substituents second in order.

For use of the above organic carbonyl compounds as driers it is most convenient that they be dissolved in organic solvents which are miscible with the drying oil containing vehicles into which they are to be compounded.

Of the useful aliphatic aldehydes most are fairly completely soluble in mineral spirits and varnish maker's naphtha, and because of their solubility in a common solvent used in the paint and varnish maker's art have inherent advantage in respect to solubility.

The other group of carbonyl containing compounds containing an aromatic nucleus are more difficultly soluble, but for the greater part can be solubilized in aromatic solvents, e. g., toluene and xylene, occasionally employing in conjunction therewith, small amounts of an alcohol, e. g., ethyl, isopropyl and butyl alcohol, to aid solubility.

Specific compounds such as β-methyl umbelliferone are quite insoluble in most organic solvents and blends of ketones and alcohols were resorted to (e. g., butyl alcohol and methyl ethyl ketone) and found useful for solubilizing purposes in this specific instance.

While it is preferable that the driers be prepared in concentrated form by dissolving the effective carbonyl compounds in suitable solvents prior to use, it is not essential to resort to this step as they may also be directly incorporated in the ranges useful in the coating compositions described.

In Table I which follows, the general character of the test vehicles are described in the first column. The second column lists the compounds which are found to have observable drier activity. The third column lists the percentage of lead

(as the metal) in the standard and the percentage of the purely organic drier compared therewith. In the last column observations are recorded as to the result obtained by comparison with standard films containing cobalt, lead and manganese driers.

It is obvious that more or less in quantity of the drier tested may effect the rate of dry within the limits of proportion herein defined. Above 2% of drier is not appreciably more effective than 1.75% and 2% is therefore an upper limit dictated by optimum performance.

Table I

COMPARISON OF ORGANIC COMPOUNDS USED IN PLACE OF LEAD DRIERS

Vehicle	Compound Substituted	Percent Used	Comparison with Standard Cobalt, Lead, and Manganese Driers
maleic-rosin-soya bean oil oil length=52% N. V. M. acid value=10–12 viscosity=T (Gardner-Holdt)	vanillin	1.64	faster dry.
	p-hydroxy propiophenone		Do.
	β-methyl umbelliferone		Do.
	2-ethyl hexaldehyde		Do.
	cinnamic aldehyde		Do.
	3,5,5-trimethyl hexaldehyde		Do.
	octa-decenyl aldehyde		slightly slower.
	n-decyl aldehyde		Do.
	p-hydroxy benzaldehyde		Do.
	benzaldehyde		not as effective.
	salicylaldehyde		Do.
pentaerythritol phthalate-pentaerythritol rosin linseed oil modified alkyd varnish oil length=56% N. V. M.	β-methyl umbelliferone	0.93	faster than tandard.
	p-hydroxy benzaldehyde		Do.
	vanillin		Do.
	octa-decenyl aldehyde		Do.
	2-ethyl hexaldehyde		slightly slower.
	p-hydroxy propiophenone		Do.
	2-hydroxy-5-chlorobenzaldehyde		Do.
pentaerythritol-phthalate linseed-soya bean oil modification oil length=58% N. V. M. acid value=5–6 viscosity=X (Gardner-Holdt)	2-ethyl hexaldehyde	0.735	faster.
	p-hydroxy benzaldehyde		Do.
	3,5,5-trimethyl hexaldehyde		Do.
	n-decyl aldehyde		slightly slower.
	cinnamic aldehyde		Do.
	citronellal		Do.
	salicylaldehyde		Do.
	p-hydroxy propiophenone		Do.
pentaerythritol-rosin linseed oil vehicle oil length=66% N. V. M. acid value=3–6 viscosity=I (Gardner-Holdt)	vanillin	0.5	faster.
	p-hydroxy benzaldehyde		Do.
	p-hydroxy propiophenone		Do.
	octa-decenyl aldehyde		Do.
	β-methyl umbelliferone		Do.
pentaerythritol-glycerine linseed-soya modification oil length=73% N. V. M. acid value=3.6–7.2 viscosity=T (Gardner-Holdt)	2-ethyl hexaldehyde	0.93	faster.
	β-methyl umbelliferone		Do.
	octa-decenyl aldehyde		slightly slower.
	p-hydroxy propiophenone		Do.
straight drying oil heat bodied+alkali refined oil as used in outside house paint	p-hydroxy propiophenone	0.31	equal to standard.
	p-hydroxy benzaldehyde		slightly slower.
	2-ethyl hexaldehyde		slower.
	salicylaldehyde		Do.
	anisaldehyde		Do.

It has further been observed upon periodic examination and testing of the vehicle-drier combinations described in Table I that in some instances an initially very high peak of drier activity will level off to some extent. However, the change by comparison with the compositions containing the lead driers and the identical vehicles has been relatively insignificant and the aging tests so far indicate no instability problems due to the substitution of the driers as indicated in the disclosure.

While the research leading to the discovery of the above described purely organic compounds was conducted with the idea in mind of substitutions for lead soaps or driers in drying oil modified coating compositions, it is apparent that the compounds described need not necessarily be used in conjunction with cobalt and manganese driers, but may be used either alone or in combination with each other where it is expedient to eliminate all metallic drier combinations. However, as is preferable in the art today, combinations of driers will be found useful.

A divisional application, filed September 5, 1951, U. S. Serial No. 245,266, is directed to the aliphatic carbonyl compounds herein described as useful as siccative catalyst in drying oil modified products.

Having described the invention, we claim:

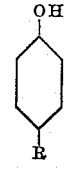
1. A composition of matter which comprises in combination an organic film forming agent containing drying oil fatty acid groups and an aromatic metal free organic drier catalyst selected from the group consisting of β-methyl umbelliferone, para-hydroxy benzaldehyde and para-hydroxy propiophenone.

2. A drier catalyst in combination with an organic coating composition containing drying oil fatty acid groups, said drier comprising β-methyl umbelliferone.

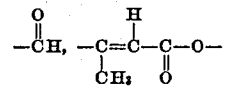
3. A drier catalyst in combination with an organic coating composition containing drying oil fatty acid groups, said drier comprising para-hydroxy benzaldehyde.

4. A drier catalyst in combination with an organic coating composition containing drying oil fatty acid groups, said drier comprising para-hydroxy propiophenone.

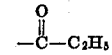
5. A drier catalyst in combination with organic coating compositions containing drying oil fatty acid groups, said drier comprising a para substituted single aromatic ring compound characterized by the structure



where R is a carbonyl containing radical selected from the group consisting of



and



CHARLES A. COFFEY.
RUSSELL T. RYAN.
LYNWOOD N. WHITEHILL.

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