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ORGANIC DRIERS IN ORGANIC FILM FORMING COMPOSITIONS

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

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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 preceding 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 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 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 non-metallic 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 or 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 the table.

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.

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.—Comparison of organic compounds used in place of lead driers

Vehicle	Compound substituted	Comparison with standard cobalt, lead and manganese driers
Maleic-rosin-soya bean oil; oil length, 52% NVM; acid value, 10–12; viscosity-T (Gardner Holdt).	2-ethyl hexaldehyde	Faster dry.
	Cinnamic aldehyde	Do.
	3,5,5-trimethyl hexaldehyde	Do.
	Octa-decenyl aldehyde	Slightly slower.
	n-Decyl aldehyde (1.64% of above used)	Do.
Pentaerythritol; phthalate-pentaerythritol; rosin linseed oil modified alkyd oil length, 56% NVM.	Octa-decenyl aldehyde	Faster than standard.
	2-ethyl hexaldenyde (0.93% of above used)	Slightly slower.
Pentaerythritol-phthalate; linseed-soya bean oil modification; oil length, 58% NVM; acid value, 5–6; viscosity-X (Gardner Holdt).	2-ethyl hexaldehyde	Faster.
	3,5,5-trimethyl hexaldehyde	Do.
	n-Decyl aldehyde	Slightly slower.
	Cinnamic aldehyde (0.735% of above used)	Do.
Pentaerythritol-rosin linseed oil vehicle; oil length, 66% NVM; acid value, 3–6; viscosity-I (Gardner Holdt).	Octa-decenyl aldehyde (0.5% of above used).	Faster.
Pentaerythritol-glycerine linseed-soya modification; oil length, 73% NVM; acid value, 3.6–7.2; viscosity-T (Gardner Holdt).	2-ethyl hexaldeayde	Faster.
	Octa-decenyl aldehyde (0.93% of above used)	Slightly slower.
Straight drying oil; heat bodied+alkali refined oil as used in outside house paint	2-ethyl hexaldenyde (0.31% of above used)	Slower.

Among the non-metal containing organic compounds tests 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:

Carbonyl compounds—aliphatic aldehydes:
Octa-decenyl aldehyde
2-ethyl hexaldehyde
n-Decyl aldehyde
3,5,5-trimethyl hexaldehyde
Citronnellal
Cinnamic aldehyde

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 as ortho in position to the carbonyl containing group, improvement over the meta substitued 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. These compounds are described in copending application Serial No. 147,334, filed March 2, 1950, now U. S. Patent No. 2,631,944, issued March 17, 1953 of which this case is a division thereof.

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.

While it is preferable that the driers to 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 the table 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 and 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

It has further been observed upon periodic examination and testing of the vehicle-drier combinations described in the table 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.

Having described the invention, we claim:

1. A composition of matter which comprises in combination a siccative organic film forming coating composition containing drying oil fatty acid groups and a metal free drier catalyst, said drier selected from the group of aliphatic aldehydes consisting of 2-ethyl hexaldehyde, cinnamic aldehyde, 3,5,5-trimethyl hexaldehyde, octa-decenyl aldehyde, n-decyl aldehyde and citronellal.

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

3. A drier catalyst in combination with an organic coating composition containing drying oil fatty acid groups, said drier comprising cinnamic aldehyde.

4. A drier catalyst in combination with an organic coating composition containing drying oil fatty acid groups, said drier comprising n-decyl aldehyde.

5. A drier catalyst in combination with an organic coating composition containing drying oil fatty acid groups, said drier comprising octadecenyl aldehyde.

6. A drier catalyst in combination with an organic coating composition containing drying oil fatty acid groups, said drier comprising citronellal.

7. A composition of matter which comprises in combination a siccative organic film-forming coating composition containing drying oil fatty acid groups and as a drier catalyst therefor a metal free unsubstituted aliphatic aldehyde containing from seven to eighteen carbon atoms.

8. A composition of matter which comprises in combination a siccative organic film-forming coating composition containing drying oil fatty acid groups and as a

drier catalyst therefor a metal free unsubstituted aliphatic aldehyde containing from seven to eighteen carbon atoms in which said aldehyde group is attached to the terminal carbon atom of said aliphatic chain.

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