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DRIER ACCELERATORS

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5 Claims. (Cl. 106—264)

The invention relates to improved drier compositions.

The conventional driers in drying oil compositions are mixtures of metallic soaps, of which the soaps of cobalt, manganese and iron are the most important primary driers necessary to accelerate the drying process and to produce a dry tack-free surface in a short time. In combination with said primary driers, metal soaps of other metals, such as those of lead and calcium, are used as secondary driers, which have no drying properties of themselves but serve to dry the film through.

The soaps of cobalt have been considered the preferred driers because they are least liable to discolor the obtained coatings. However, as cobalt is not available in sufficient amounts and is expensive, manganese and iron soaps are used as substitutes, which are fairly good driers but have the drawback of imparting a dark color or stains to coatings. Therfore, it is desirable to limit the amount of such driers in drying compositions.

It is known that the amount of driers can be reduced by the addition of certain organic compounds. The compounds proposed for this purpose are, however, difficult to prepare and have other disadvantages.

It is a principal object of the invention to provide low cost drier combinations of a lowered metal content with organic compounds, which have excellent drying and post-drying properties and do not increase the color, heat, light and moisture sensitivity and brittleness of the coatings.

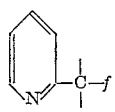
Another object is to provide drier compositions consisting essentially of a manganese and/or iron drier and an organic drying accelerator, which have the same drying properties as cobalt driers.

Other objects and advantages will become apparent from the specification and claims.

We have found that organic compounds in which trivalent nitrogen is conjugated with a resonating system which contains an oxygen containing group, such as hydroxyl, alkoxy, or carboxyl, constitute excellent accelerators for primary driers and allow of considerably reducing the amount of metal drier to be incorporated in the drying oil composition.

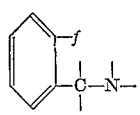
Such organic compounds are heterocyclic compounds either of the type

(1)



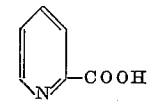
or of the type

(2)

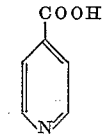


wherein *f* designates the oxygen containing group. If *f* is an OH group, it will be seen that the compounds have a configuration in which the nitrogen is in a position

capable of forming a five or six-membered ring by chelation with a metal. This configuration appears to be critical for the desired effect of our novel drying accelerators. For instance, we have found that picolinic acid of the formula



is an excellent drying accelerator, whereas with isonicotinic acid of the formula

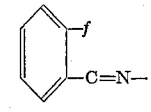


no accelerating effects could be observed.

Compounds conforming to Formula 1 are, e. g. picolinic acid and the esters thereof, 8-hydroxy quinoline, and others.

Compounds conforming to Formula 2 are, for instance, ortho-dimethylaminomethyl parabutylphenol and the corresponding paraoctylphenol. Particularly efficient accelerators are compounds of the Formula 2 in which the nitrogen is bound by two of its valances to the carbon atom, i. e. Schiff's bases of the formula

(2a)



Examples of such suitable Schiff's bases are, for instance, N,N'-disalicylalethylenediamine, N,N'-disalicylalorthophenylene - diamine, N - salicylalpropylamine, and similar compounds; also suitable is e. g. N,N'-disalicylalpropylenediamine.

The accelerators are added preferably in an amount of about 0.02 to about 2 moles per 1 mole of the metal of the drier composition, whereby the drier may be present in the form of the naphthenate, linoleate, oleate, 2-ethylhexoate, resinate, or similar salt of manganese, iron, or lead.

The following examples are given to illustrate in more detail the effect of the novel drying accelerators in manganese drier compositions, which are particularly important from a practical point of view. It is to be understood that corresponding effects are observed in combinations containing other metal driers, where an increased drying rate is obtained with limited amounts of the drier by addition of the accelerator.

For the tests, the standard linseed oil solutions of manganese or iron naphthenate were prepared by the addition of the requisite amount of 6% manganese or iron drier to a raw linseed oil to yield solutions containing 0.10% of the metal. These standard solutions were diluted with the quantity of linseed oil required to produce solutions containing 0.04 to 0.05 of the desired metal content. Other portions of the solutions were diluted with linseed oil solution containing the accelerator in varying concentrations.

The thus prepared formulations were evaluated by comparing their Gardner drop times with that of an 0.03% cobalt stock solution prepared in a fashion similar to the preparation of the manganese and iron standard solutions. The Gardner drop time is a means of characterizing the extent of oxidation of a film in terms of the time required to attain a certain consistency.

On viewing the following tables, it will be noted that the Gardner drop times vary for standard solutions having the same composition. The reason is that the drying

rates for similar solutions vary from day to day because they are subject to many variables including temperature, humidity, illumination, air flow, age of the sample, thickness of the film, and others. In order to obtain reliable comparative figures, it is therefore not permissible to make a single blank test and refer all the following tests to said blank test but it is necessary to run a check test with every single group of tests, which we have done.

Comparison of some of the formulations also was done according to U. S. Government Specifications TTP–141B, for Dried Hard, in which the maximum pressure of the finger does not leave a permanent mark.

Results of the evaluations of various accelerators and concentrations are given in Table I, wherein the different accelerators have been designated as follows:

N,N'-disalicylalethylenediamine ..... A
N,N'-disalicylalorthophenylenediamine ..... B
Picolinic acid C
Methyl picolinate ..... D
Ortho-dimethylaminomethyl para-octylphenol ..... E
Ortho-dimethylaminoethyl para-butylphenol ..... F
8-hydroxyquinoline ..... G
N-salicylalpropylamine ..... H

In the tables, the first column indicates the type of accelerator used, the second column gives the amount of accelerator in moles per mole of the metal, and the third column indicates the metal concentration.

The first table shows the improvement in drying times measured as Gardner drop times.

TABLE I

Acceleration of catalysis

Accelerator		Metal, Percent	Gardner Drop Time (Hours)
Type	Amount		
		0.04 Mn	6.2
A	0.1	0.04 Mn	2.7
A	0.2	0.04 Mn	2.7
A	0.4	0.04 Mn	3.0
A	0.8	0.04 Mn	4.2
A	2.0	0.04 Mn	4.4
		0.05 Mn	5.6
B	0.2	0.05 Mn	4.4
B	2.0	0.05 Mn	3.0
		0.05 Mn	7.1
C	2.0	0.05 Mn	4.0
		0.04 Mn	6.8
D	2.0	0.04 Mn	4.2
		0.04 Mn	9.3
E	2.0	0.04 Mn	4.8
		0.04 Mn	9.3
F	2.0	0.04 Mn	4.8
		0.04 Mn	7.0
G	2.0	0.04 Mn	4.3
		0.04 Mn	6.8
H	2.0	0.04 Mn	4.2
		0.04 Mn	7.0
		0.05 Fe	30.0
A	2.0	0.05 Fe	7.6
B	2.0	0.05 Fe	10.3
D	2.0	0.05 Fe	10.0
H	2.0	0.05 Fe	8.8

It should be noted that in the case of iron, the drying time of the blanks was frequently more than 30 hours. The time of 30 hours has been inserted because drying times greater than 30 hours cannot be read with precision. Therefore for iron catalysts, the effect of the accelerators is actually still better than indicated by the figures given in the table.

Table II shows the results of tests made according to U. S. Government Specification TTP–141B for one of the accelerators. Similar results were obtained with other drier-accelerator combinations according to the invention.

TABLE II

Accelerator		Metal, Percent	Dried Hard Time (Hours)
Type	Amount		
		0.04 Mn	10.8
A	0.1	0.04 Mn	4.3
A	0.2	0.04 Mn	3.8
A	0.4	0.04 Mn	3.8
A	0.8	0.04 Mn	2.5

In order to show the influence of the metal concentration, the following table is given for a constant 0.2 amine to metal ratio at increasing metal concentrations.

TABLE III

Accelerator		Metal, Percent	Gardner Drop Time (Hours)	Improvement in Percent
Type	Amount			
		0.02 Mn	12.0	
A	0.2	0.02 Mn	5.0	170
		0.04 Mn	7.3	
A	0.2	0.04 Mn	3.3	120
		0.06 Mn	6.0	
A	0.2	0.06 Mn	3.0	100

The influence of the vehicle is shown in Table IV. The effect of the accelerator is particularly noticeable with vehicles which have not very good drying properties of themselves.

All the tests were made with a Mn content of 0.04% and with the accelerator A. In the column indicating the Gardner drop time, the second figures designate the drop time of the blank test without accelerator.

TABLE IV

Vehicle	Accelerator-Metal Ratio	Gardner Drop Time (Hours)	Improvement, Percent
Alkali-refined linseed oil	0.10	3.0 vs. 8.0	160
White refined linseed oil	0.04	3.8 vs. 8.0	110
Extracted linseed oil	0.10	6.3 vs. 13.8	120
Raw linseed oil	0.20	3.3 vs. 7.3	120
Expelled linseed oil	0.30	4.3 vs. 8.7	100
Aged raw linseed oil	0.20	3.7 vs. 6.0	60

We may use the drier composition in film-forming bases conventionally employed in paints, varnishes, enamels, printing inks and linoleum print paints containing a drying or semi-drying oil fatty acid radical. The film-forming base contains about 0.01 to 1 percent, preferably 0.025 to 0.1 percent by weight of our new drier composition, based upon the weight of the metals and upon the polymerizable drying oil or semi-drying oil content of the base.

The composition of such film-forming bases is well known in the art. The bases may include the usual pigments, extenders and fillers, and are prepared from drying or semi-drying oils, such as linseed oil, dehydrated castor oil, and the like, from esters of drying or semi-drying oil fatty acids with polyhydric alcohols, from drying or semi-drying oil modified resins, particularly modified alkyl or phenolic resins, from modified rosin esters and natural resins.

What we claim is:

1. A drier composition comprising as a primary drier a soap of a metal selected from the group consisting of iron, lead, and manganese, and as a drying accelerator an aromatic tertiary amine selected from the group consisting of Schiff's base compounds selected from the group consisting of salicylal and disalicylal lower alkyl amines

and diamines and the orthophenylene diamine derivatives thereof.

2. A drying oil composition containing an organic film-forming agent selected from the group consisting of drying and semidrying oils, esters of drying and semidrying oil fatty acids with polyhydric alcohols, alkyd resins, phenolic resins, neutral resins, and rosin esters, said alkyd resins, phenolic resins, natural resins, and rosin esters being drying oil and semidrying oil modified, and as a drier a drier composition as defined in claim 1.

3. A drier composition containing as a primary drier a manganese soap, and as a drying accelerator N,N'-disalicylalethylenediamine.

4. A drier composition comprising as a primary drier a soap of a metal selected from the group consisting of iron, lead, and manganese, and as a drying accelerator an N-salicylalalkylamine which contains less than 5 C atoms in the alkyl group, in an amount effective to accelerate the drying of said drier soap.

5. A drier composition comprising as a primary drier a soap of a metal selected from the group consisting of iron, lead, and manganese, and as a drying accelerator an N,N^1-disalicylalalkylenediamine, wherein the alkylene group connecting the N and N^1 atom has a carbon chain of less than 5 C atoms, in an amount effective to accelerate the drying of said drier soap.

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