Driers for Waterborne Coatings

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There are 17 different metals used in driers for coatings. The role of these various metals in the promotion of the drying of coatings is described. Suggestions are given concerning the choice of which metal driers to use in waterborne coatings and what concentrations are typically used. Specific examples are described to help illustrate these choices. Several new water-reducible driers are presented together with their benefits and advantages compared to the more commonly used driers.

Probably the oldest and most common air-driable waterborne coatings are alkyd emulsions. Today there are many other emulsifiable oil-modified (i.e., air-driable) resins such as polyolefins, polyurethanes, phenolic-modified alkyds, styrenated alkyds, silicone-modified alkyds, epoxy esters, and acrylic-modified alkyds. Then there are the blends of two to as many as five different water-reducible resins. Some resins in these blends are dispersions and some are emulsions; some require driers and some do not. Design of drier packages for these various waterborne coatings is usually done on a case-by-case basis because of the diversity of water-reducible resins and because the drier package is strongly dependent on the nature of each individual coating product. This is not the case with solventborne coatings where the same drier package can be used successfully in a variety of solventborne coatings products. Fortunately there are some guidelines to help the formulator of waterborne coatings choose candidate driers to test. Recently a number of new emulsifiable driers have been introduced, which expand our capability for solving drier problems in complex waterborne coatings.

EXPERIMENTAL

The dry times reported in this work were determined in an environmental chamber set at 25°C (77°F) and 50% relative humidity using 12-hour Gardner improved circular dry time recorders. The wet paint films were cast on sealed Leneta charts using a Baker adjustable gap bar set at 4 mils. All of the driers used in this work were emulsifiable concentrates. After the driers were added to the paint samples, the samples were shaken on a Red Devil paint shaker for about 15 min and then allowed to stand overnight before being shaken for another 15 min before casting the wet films. Typically, the variables usually studied are the drier concentrations, the temperature, the relative humidity, and the wet film thickness.

DISCUSSION

What is a Drier?

A drier for coatings is a metal carboxylate which catalyzes or performs or promotes the crosslinking of resin polymers or drying oils. Driers are often divided into three classes:

(1) Catalytic driers are sometimes called top driers, surface driers, or oxidative driers. There are five commercial catalytic driers: Co, Mn, V, Ce, Fe.

(2) Crosslinking driers are sometimes called through driers, polymerizing driers, or coordination driers. There are eight commercial crosslinking driers: Pb, Zr, La, Nd, Al, Bi, Ba, and Sr.

(3) There are four other commercially used metal carboxylates that do not normally perform a drying function, but they do affect the rate-of-dry by interacting with the catalytic driers. These four are sometimes called auxiliary driers, promoters, or coordination driers. The four are: Ca, K, Li, and Zn. (The first three usually increase the rate of top dry and the zinc usually inhibits the top dry.)

The function of the top driers is to catalyze the decomposition of the peroxides formed by the reaction of the oxygen in the air with the resin or drying oil. This oxidative or free-radical chemistry leads to the formation of some direct polymer-to-polymer crosslinks (top drying) and also to the formation of hydroxyl groups and carbonyl groups on the resin polymer and on the drying oil. The hydroxyl groups are then available for the through drying or crosslinking by the through driers, which form oxygen-metal-oxygen bridges or crosslinks between the polymers. Carboxylic acid groups on the resin may also be used by through driers to make the oxygen-metal-oxygen crosslinks.

Driers for Waterborne Coatings vs. Solventborne Coatings

The presence of large volumes of water changes the drying chemistry of coating resins. Water can act as a chain-transfer agent in free-radical chemistry, which can markedly slow the rate of the desired free-radical reactions. Indeed, it is known that more catalytic driers are needed in waterborne coatings compared to similar solventborne coatings. For example, most solventborne coatings can be dried adequately with 0.02-0.06% cobalt, but most waterborne coatings require 0.10-0.15% cobalt. (The convention for expressing drier concentration is to express it as % metal based on the % vehicle solids or curable resins plus drying oils.)

Another major difference is that through driers are often less effective in waterborne coatings than in solventborne coatings. Indeed, in many waterborne coatings no through driers are needed at all, whereas in most solventborne coatings a through drier is vital to a good drying system. For example, many waterborne coatings may be dried with 0.10% cobalt alone.

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Table 1—McWhorter's 74-7495, Chain-Stopped Alkyd

% Co	% Nd	% Ca	% Bipy	Dry Time, Hr. Through	Dry Time, Hr. Hard	
0.04	—	—	0.014	>12	—	
0.04	—	—	0.07	4	9.5	
0.04	0.3	—	0.07	6	6	
0.04	0.3	—	0.014	7	9	
0.04*	—	0.2	0.014	5.5	8.5	*plus 0.2% Zr
0.05	—	0.2	0.018	4	11	
0.10	—	—	0.036	3	5	
0.05**	—	—	0.032	4	5.5	**plus 0.05% Mn

Table 2—Reichhold's Kelsol 3912 Alkyd

% Co	% Mn	% Nd	% Ca	%Zr	% Bipy	Dry Time, Hr.
0.05	—	—	—	—	0.02	>12
0.10	—	—	—	—	0.04	10
0.15	—	—	—	—	0.21	7
0.05	0.05	—	—	—	0.034	10.5
0.05	—	0.3	—	—	0.02	10.5
0.05	—	—	—	0.2	0.02	>12
0.05	—	—	0.2	—	0.02	Gel

Recent Developments in Water-Reducible Driers

For many years the only water-reducible driers used commercially were cobalt, manganese, calcium, and airconium carboxylates. Because of the increasing complexity of waterborne coatings, several new water-reducible driers have recently been introduced to give the coatings formulators more tools to work with to provide adequate drying and other desired properties for waterborne coatings. Two rare earth driers are now available in a water-emulsifiable form, namely lanthanum and neodynium. These two through driers have been used successfully for years in conventional and high-solids solventborne coatings; and, now they are available for use in waterborne coatings. Vanadium octoate has been used for years in difficult-to-dry solventborne coatings, especially for thick film applications. Now a water-emulsifiable form of vanadium octoate is available. The vanadium is a catalytic drier and is usually used with cobalt at about the same concentration as the cobalt.

Light-colored manganese driers are another new development. In the past, the major problem with using manganese driers was their dark brown color. Recently, a way to make light-colored manganese carboxylates was discovered. Manganese is an effective catalytic drier in many waterborne coatings. It is interesting to note that manganese driers are effective in drying most alkyd emulsions, but they often inhibit the dry with solventborne alkyds.

Two seldom-used driers, cerium and bismuth, have recently been made available as water-emulsifiable concentrates. Water-emulsifiable zinc has been available for many years.

Drier Accelerators

There are two drier accelerators that are used extensively commercially, namely 2,2′-bipyridyl (Bipy) and 1,10-phenanthroline. Both are used in solventborne and in waterborne coatings in order to decrease the dry time. They function by complexing with the metals in the catalytic driers by forming chelates. This apparently increases the activity of the metal toward decomposing peroxides. There are several other advantages one can obtain when using an accelerator.

In waterborne coatings, hydrolysis of the driers can lead to a loss-of-dry upon storage of the coating. Some protection from this hydrolysis is enjoyed in the presence of an accelerator due to the complex formation. In both waterborne and solventborne coatings a reduction in the loss-of-dry due to adsorption of

Table 3—Reichhold's Kelsol 3906 Alkyd

% Co	% Mn	% La	% Nd	% Ca	% Zr	% Bipy	Dry Time, Hr.
0.04	—	0.3	—	—	—	0.014	4.5
0.04	—	—	0.3	—	—	0.014	10.5
0.04	—	—	—	—	—	0.074	6
0.04	—	0.3	—	—	—	0.074	7.5
0.04	—	—	0.3	—	—	0.074	7
0.05	—	—	—	—	—	0.02	>12
0.05	—	—	—	0.2	—	0.02	>12
0.05	—	—	—	—	0.2	0.02	10
0.05	—	—	—	0.2	0.2	0.02	6
0.05	0.02	—	—	—	—	0.026	9
0.05	0.05	—	—	—	—	0.034	8.5
0.05	0.05	—	—	—	—	0.094	6.5
0.10	—	—	—	—	—	0.04	9

Table 4—White Paint and Amoco's 151 Alkyd[a]

% Mn	% Ca	% Zr	% Bipy	Dry Time, Hr.
—	—	—	0.04	20
0.10	—	—	0.08	6
0.10	—	—	0.17	6
—	0.10	0.10	0.04	16
—	0.20	0.20	0.04	11
—	0.20	0.20	0.13	8

(a) Each test contains 0.10% Co.

the metallic drier onto pigments is also enjoyed in the presence of an accelerator for the same reason. Another advantage is that a significant reduction in the yellowing-upon-aging is obtained through the use of an accelerator, especially in high-solids coatings.

Typical Drier Systems for Waterborne Coatings

Here are some examples of some successful typical drier systems for waterborne coatings:

0.10-0.15% Cobalt (Co)

0.10% Co + 0.1% Bipy

0.05% Co + 0.05% Mn

0.05-0.10% Co + 0.2% zirconium or lanthanum

0.05% Co + 0.2% zirconium + 0.3% calcium

0.10% Mn + 0.1% Bipy

Some Reactions that Occur During the Air Drying of Coatings

The process of the air drying of resins and drying oils can be described as consisting of five stages:

(1) Induction Period. During this first stage, the oxygen in the air is migrating to the wet paint film and is dissolving in the wet film and is migrating to unsaturated sites in the resin or drying oil. (The rate of drying is typically mass transfer limited.)

(2) Peroxide Formation. The molecular oxygen is converted to hydroperoxides and peroxides on the resin or drying oil.

(3) Peroxide Decomposition. The catalytic driers catalyze the homolytic decomposition of the peroxides. During this stage some chain-to-chain crosslinks are formed which gives rise to some increase in the viscosity and some top drying. Also during this stage, hydroxyl groups are being formed.

(4) Through Drying. The through driers crosslink the resin and drying oil at the hydroxyl and carboxyl groups. During this stage the viscosity increases markedly to yield a dried film.

(5) Degradation. This oxidative drying process continues as long as there are unsaturated sites available. This can lead to checking and brittleness.

A few of the significant reactions that occur during the air drying of an unsaturated resin or drying oil are as follows:

Peroxide Formation:

R–H (allylic) + O2 = R* + HOO*

R* + O2 = ROO*

ROO* + R'H (allylic) = ROOH + R'*

Peroxide Decomposition and Regeneration of the Metal Catalyst:

ROOH + Co++ = RO* + HO– + Co+++

ROOH + Co+++ = ROO* + H+ + Co++

RO* + Co++ = R = O (carbonyl) + Co+++

R–H + Co+++ = R* + H+ + Co++

Chain-to-Chain Crosslinking:

RO* + –CH = CH– = RO–CH–C*H–

R* + –CH = CH– = R–CH–C*H–

Through Drying:

RO* + R'H = ROH + R'*

ROH + M(Carboxylate)2 = RO - M - OR + 2 Carboxylic acid

Adding Driers to Waterborne Coatings Products

In the manufacture of waterborne coatings, it is usually best to add the driers last with good agitation. If one encounters problems in adequately blending the driers into the coating product, there are several things that are sometimes done to help improve the mixing efficiency. One can dilute the driers with an equal volume of a suitable solvent, such as a glycol ether, before adding the driers to the coating product. Or, one can add additional surfactant to the drier before adding to the coating product. Surfactants with HLB's of 10-15 should be satisfactory; and, only about five percent surfactant, based on the drier product, should be sufficient. Pre-mixing the driers with a water-emulsifiable calcium drier sometimes is beneficial.

RESULTS

Some examples of the dry time results from six commercial waterborne alkyds are shown in *Tables* 1-6. These results illustrate the variable activity of some water-emulsifiable driers with a variety of resins. In *Table* 1, the test with 0.1% cobalt gives the best dry time, but we can see that replacing half the cobalt with manganese yields a similar result. This is a common result for many alkyd emulsions. Reducing the amount of cobalt to 0.04% yields an unacceptable long dry time, but simply adding additional bipyridyl complexing agent to the small amount of cobalt greatly reduces the dry time. The addition of Nd or the addition of the combination of Zr and Ca each yields better drying than 0.04% cobalt alone, but not as good as the 0.1% Co case. It is interesting to note that the addition of calcium alone to 0.05% Co yields an excellent "through" dry, but not a good "hard" dry.

In *Table* 2, once again the 0.1% Co appears to yield the best dry time, except for a case where 0.15% Co is used with a large amount of bipyridyl. Once again replacing half the cobalt with manganese yields about the same dry time as cobalt alone. The neodymium system gave a good dry time and should be considered further for this particular resin. On the contrary, the addition of zirconium was ineffectual and the addition of calcium resulted in gel formation, probably due to the instability of the emulsion in the presence of the calcium drier, even though the calcium drier was added as an emulsifiable concentrate.

In *Table* 3, the best drier system for this resin was 0.04% cobalt with 0.3% lanthanum. (Interestingly, another rare earth, neodymium, was not very good with this resin). Two second-best systems were either 0.04% Co with extra bipyridyl or a Co/Ca/Zr system. Cobalt

Table 5—Cook Composites' Chempol 10-0097 Alkyd

% Co	% Zr	% Ca	% Bipy	Dry Time, Hr.
0.10	—	—	0.04	>12
0.05	0.3	—	0.02	>12
0.05	—	0.3	0.02	7

Table 6—McWhorter's Aquamec 1100, Acrylic Alkyd

% Co	% Zr	% Ca	% Bipy	Dry Time, Hr.
0.10	—	—	0.04	7
0.05	—	—	0.02	>12
0.05	0.3	—	0.02	6
0.05	—	0.3	0.02	7

without the extra bipyridyl was not very good at all. Also, the two binary systems: Co + Ca or Co+ Zr were not very good either. The use of manganese does not appear to be very advantageous with this resin.

In *Table* 4, Co/Mn systems were much better than cobalt alone. Also the Co/Ca/Zr system with additional bipyridyl was effective. In *Table* 5 a Co/Ca system was much better than a Co/Zr system or 0.1% Co alone. In *Table* 6 a Co/Ca system was about the same as a Co/Zr or 0.1% Co alone.

SUMMARY

Often the best drier system for alkyd emulsions is simply 0.1% cobalt (as metal, based on the vehicle solids), even though one has a choice of 17 different metal driers available commercially. It is usually advantageous to provide a complexing agent, like 2,2'-bipyridyl, along with the cobalt. Indeed, most commercially available catalytic emulsifiable driers are offered with complexing agents. Many commercial waterborne, air-driable coatings products contain several different resins, which complicates the drying process and sometimes gives rise to the need to use several driers in addition to the cobalt. Recently a number of new water-remulsifable driers have become available for use with "problem dry" coatings. The illustrative examples of dry-time testing with several alkyd emulsions demonstrate that the addition of non-catalytic driers like Zr, Ca, and rare earth sometimes reduces the dry time, but sometimes they are detrimental or not effective. These examples also show that the choice of the best drier system is dependent on the nature of the resin.