Metal Carboxylates for Coatings – Driers / Siccatives

Metal carboxylates are more commonly referred to as driers or siccatives. They are an organometallic salt, formed by the reaction of a metallic raw material and organic acid(s) dissolved in a hydrocarbon solvent. When added to alkyd based paints they markedly reduce the drying times.

Driers / Siccatives are catalysts The metal is responsible for the catalytic action of reducing the drying time.

Carboxylate Acid Types

Natural

- Naphthenates
- Fatty acids (unsaturated oleates)
- Tallates

Naphthenic acid has been traditionally used to make driers. Naphthenic acid is a petroleum derivative and is not a pure chemical compound and as such can be variable in its quality. Quality can be improved by special chemical processes which improves the overall chemical integrity. Naphthenates are particularly favourable when lower water solubility of the carboxylate is required.

Synthetic

- 2-ethylhexanoate (octoate, C8)
- Neodecanoate (C10)
- Isononanoate (C9)

Synthetic acids are used in place of naturally occurring acids as they offer low odour, enable higher metal contents and consistent quality.

Chemistry Metal Carboxylates are classed as:

- O Neutral
- Acidic (more commonly classesd as neutral)
- O Basic
- O Overbased refers to the use of CO₂

Primary driers:

Act as oxidation catalysts, as their metal soaps exhibit more than one oxidation state. Primary driers catalyse cross linking of the resin and in the process hydroxyl, carbonyl and carboxylic groups are formed

Through driers:

Ensure that a coating dries at a uniform rate throughout the body of the film. Primary driers without the presence of through driers would mainly dry the surface of the film, whilst the coating underneath would remain wet. Through driers are used to ensure that the coating dries at a uniform rate throughout the body of the film not just at the surface.

Through driers link fatty acid chains via oxygen-metal-oxygen bridges leading to cross-links.

Auxiliary driers:

Modify the effect of other driers but do not demonstrate any drying action on their own.



ZirconiumNot as effective as lead but is less toxic and was the first identified alternative to lead.
Zirconium has replaced lead in a number of countries.

Lithium Effective at low temperatures. In specific resins, dosing above a critical load of 0.02% on resin leads to premature film cracking.

Strontium

Now offered as a replacement for zirconium and lead. Has no known toxicity unlike zirconium and lead.

Cerium	More active than lead and effective at low temperatures and high humidity. Cerium can cause yellowing of the film and excess addition can cause skinning. Pure cerium is often too expensive for coatings formulations and a more cost effective blend of rare earth metals is commonly used offering the same benefits. Cerium can be considered as a primary drier in some systems.
Neodymium	Effective at low temperatures and high humidity, and especially effective in drying difficult to cure high solids coatings and where improved hardness and durability are required.
Potassium	Used mainly for the curing of unsaturated polyester resins; and in water based coatings to aid solubility.
Aluminium	Highly resin specific but very effective where it is found to work. Yields large viscosity build in systems of high acid or hydroxyl number. Effective in drying difficult to cure high solids coatings. Not very effective at lower temperatures.

Auxiliary Drier Metals

Calcium keeps the film matrix open which allows more oxygen into the film and more Calcium solvent to escape early in the drying process. Calcium assists in pigment dispersion and reduces loss of dry when added in the pigment grinding stage. Barium Improves gloss and reduces loss of dry. Through dry intensified in conjunction with Cobalt. Also acts as a pigment wetting agent. Barium can have a negative impact on drying when combined with cobalt alternatives. Zinc Keeps the film open, prevents wrinkling and skinning of the film.

Calculation of Addition Rate Weight of drier required is calculated using the following equation: (% resin solids) x % metal required x batch weight % Metal of drier Solution For example: 15000 kg paint of 40% alkyd resin solids, requiring 0.06% Cobalt on resin solids will require 30 kg of Duroct[®] Cobalt 12%

The Drying Process in a Coating



All driers work through the whole of the coating Primary driers are most active at the surface where the oxygen content is the highest

Oxygen Absorption	Solvent Evaporation
Primary / Surface	Driers

Oxygen from the atmosphere is absorbed by the primary drier at the surface of the coating Solvent and MEKO evaporate

Auxiliary driers act at the surface depending on their functionality.

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Calcium opens the matrix structure to facilitate solvent evaporation and deeper oxygen penetration. Free radical process started at the surface is passed down through the film. Through driers promote drying of the body of the film.

High Solids – Low VOC Coatings / Resins

- Used to reduce the solvent.
- To reduce the solvent the resin structure is modified by reducing the amount of fatty acid, reducing the amount of unsaturation or by reducing the molecular weight.

This affects the properties.

- Resin viscosity build is different.
- Resin has a higher vellowing tendency due to lower crosslink density.
- Slower dry times due to lower mobility and lower levels of unsaturation.
- Softer films with lower durability.

Driers for High Solids – Low VOC Coatings

As well as the standard driers Dura offers a range of specialty driers:

- **Duroct[®] Lithium 2% NDA**
- DriCAT[®] 3 & 4 (Vanadium 3 & 4%) DriCAT[®] 12 (Neodymium 12%)
- DriCAT[®] 16 (Mixed metal blend)
- **DriCAT[®] 18** (Mixed metal blend)
- Dural[®] A-MS (Aluminium 7%)
- XL-Dri

These products can improve the drying when standard driers are inadequate.

Tech Brief – Driers for High-Solids Coatings

Water Borne Coatings

- They provide advantages over traditional solvent based coatings
- They are generally faster drying this can also be a disadvantage as there isn't the same control
- Alkyd based coatings still require driers

Driers for High Solids – Low VOC Coatings

The drying mechanism is very similar to that for solvent borne coatings, so the metal types used are the same. The presence of water in a coating can give many challenges for driers

- Drier incompatibility with resin
- Drier hydrolysis or seeding (calcium or zirconium)
- Resin discoloration
- Poor initial dry
- High formulation costs
- Critical recoat times
- Restricted drier addition
- Loss of dry with time

This line of driers was especially developed for use in alkyd based water borne coatings. The driers may be incorporated during the let-down operation with simple agitation. To reduce the risk of flocculation or coagulation the driers can be pre-mixed with the binder or water or glycols /glycol ethers to avoid the problems associated with drier incompatibility due to solvent polarity differences.

- Duroct[®] WR Series 6% Co, 10% Co, 6% Mn, 6% Ca and 12% Zr
- Duroct[®] Lithium WR 2% NDA VOC free drier
- Duroct[®] WDX Series 5% Co and 8% Mn
- DriCAT[®] 10 Mixed Cobalt / Potassium drier
- DriCAT[®] 506 Mixed metal blend (Co/Ba/Zr)
- DriCAT[®] 507 Mixed metal blend (Co/Li/Zr)
- DriCAT[®] 509 Mixed metal blend (Co/Ba/Zr)
- DriCAT[®] 508 Cobalt free drier
- DriCAT[®] 2705FW Cobalt free drier
- DriCAT[®] 2715FW Cobalt free drier
- DriCAT[®] 2725FW Cobalt free drier

Tech Brief – Driers for Waterborne Coatings

Ultra Low VOC Driers

Increased emphasis is currently being placed on the reduction of VOCs to reduce air pollution and the effects of greenhouse gases upon the atmosphere. As regulations demand lower VOCs, the contribution of the solvents in the driers becomes more and more important and critical to product performance.

DURA have introduced several Ultra-Low VOC driers for low VOC compliant coatings.

- DriCAT[®] 2712 12% Cobalt 2-Ethylhexanoate in Methyl Soyate
- DriCAT[®] 2508 8% Manganese 2-Ethylhexanoate in Methyl Soyate
- DriCAT[®] 2005 5% Calcium 2-Ethylhexanoate in Methyl Soyate
- DriCAT[®] 4012 12% Zirconium 2-Ethylhexanoate in Methyl Soyate

All of these driers have non-volatile / solids contents in excess of 95%.

Blends

Dura offer a variety of "Industry Standards" as well as customised blends. A pre-blended drier combination offers advantages over single metal driers; technically, the blends are pre-stabilised and as such eliminate the problems of gelling resulting from the acid/base nature of different driers. Production controls guarantee metal ratios, thus removing any performance variations associated with fluctuations in metal concentrations or ratios. Financially, one mixed drier replaces several metal driers, this reduces stock levels and working capital. There is one addition made, this simplifies the process. The addition rates are determined by the cobalt concentration.

Specialty Driers

DriCAT[®] 408 is a special cobalt-free drier catalyst for oxidatively drying urethane alkyd lacquers. Clear floor coatings based on urethane modified lacquers show mostly a dark color when cobalt is used as a drier. DriCAT 408 is a drier complex that can be combined with, for example, zirconium and calcium and will assure good drying properties of urethane alkyds while keeping the hue as light as possible.

Dural[®] A-MS (Aluminium 7%) is not a conventional drier, aluminium-modified systems do not depend on the auto-oxidative drying process alone. Aluminium complexes serve as through driers, and in such aluminium modified systems the film formation takes place through the complexing reactions between aluminium atoms and residual carboxyl and hydroxyl moieties of the resin, both present initially and formed during the auto-oxidative process. The progressive formation of such aluminium resin linkages results in corresponding depletion of free carboxyl and hydroxyl groups in the film yielding significant advantages including:

- Reduction or elimination of wrinkling especially in thicker films
- Enhanced water resistance of drier films
- Greater film hardness
- Improved gloss retention

The final cross-linked film is thus held together by a combination of covalent coordinate linkages (*through aluminium and oxygen atoms*) and covalent linkages formed through auto-oxidative reactions.

Aluminium is used in conjunction with primary driers such as like cobalt or manganese.

Cobalt Alternatives

The Evolution of Cobalt Alternatives

The search for effective alternatives to cobalt carboxylates has been on-going for decades, whether on cost or on health and safety grounds. The redox process of other commonly available metal carboxylates is much less effective than that of cobalt and as such it is necessary to "modify" the metal carboxylates to improve the metal redox process. The most noted alternatives have centred on the complexation of manganese or iron carboxylates, although other metals have often been of interest for specific applications.

The early chelating ligands were aromatic amines; namely 1,10-phenanthroline and 2,2'-bipyridyl. Amines were chosen because manganese, in particular, has an affinity to complex with nitrogen ligands due to the vacant d-orbitals. These two amines were chosen because of availability and the formation of strong complexes with the manganese carboxylates. Complexes formed with these two amines did show a faster redox process which gave drying times in coatings comparable to that of cobalt carboxylates. Although comparable drying was achieved film hardness development was always slower resulting in softer films; and the colour change, specifically dark yellowing, was much worse. These effects were a result of a low

cross-link density in the cured film. This deficiency in performance was more noticeable in the curing, or non-curing, of unsaturated polyester resins. The use of these amines has been further limited because of their known toxicity.

Aromatic amines gave a benefit to the complex because their electron density could be utilised by the manganese amine complex, but their negative effects, particularly toxicity, needed to be addressed. To this end less toxic amines based on non-aromatic cyclic and straight chain amines were investigated. Benefits in the colour performance of films were observed but, generally, there was a loss in the drying process due to the fact that the complex formed was not as strong as with the aromatic amines. To further support this process the use of additional additives, amine and non-amine, have been tried with mixed success. Those systems that have given recordable improvements in one property have seen degradation in other properties.

The natural extension of the use of straight chain amines was to use cyclic structures and of these the earliest developments were reported in the scientific literature a few years ago. These new developments were used with and without other additives to promote the redox process, and both concepts proved successful in improving the balance of drying / curing against the negative impact of poor colour performance. Unfortunately, they were still unable to provide sufficient cross-link density to give good hardness development.

Some of the most recent developments have sought to utilise technology other than that based on metal carboxylates. The departure from the classical method has resulted in systems of unreliable performance; with these technologies the differences from one system to another makes them poor choices as cobalt alternatives.

Cobalt Toxicity

Cobalt metal in all physical forms has now been reclassified as a class 1b carcinogen. Studies are ongoing, which should help to determine the appropriate carcinogenic classification of the organometallic salts of cobalt which are used as driers / siccatives.

Product Development

DURA has developed a number of effective proprietary products that are currently used in the marketplace; the most recent of which are those of the DriCAT[®] 2700F series. This new series of products has a faster more efficient redox process. This has given good drying / curing, with the required hardness development and without the negative effect of film colour degradation with time. The technology is transferrable to other metal carboxylates, and as such a range of products are in development that will be more efficient and ecologically sound.

DriCAT[®] 2700F series

- are low concentration, high activity Manganese / iron based complexed carboxylate
- do not require the addition of further non-metallic additives to boost performance
- have drying and hardness development comparable to that of cobalt driers
- have minimal effect on the long term discoloration of the finished article
- work in combination with other Dura metal carboxylates for the most effective drying / curing
- work with MEKO or MEKO alternatives as an anti-skinning agent
- REACh registered



Organic Accelerators

The two products most commonly used in this role are: 1,10-phenanthroline and 2,2'-bipyridyl. Both are aromatic amines with a high toxicity. Non-aromatic amines and amine derivatives are now being used more commonly because they have a lower toxicity but they also have a lower activity compared to aromatic amines.

The ligand functions by chelating with the metal which increases the activity of the metal toward decomposing peroxides and hence reduce drying time. The main considerations of the effectiveness in using amines are:

- The type of resin
- Temperature
- Chemical nature of the amine

Accelerators have been found to offer benefits across the complete spectrum of alkyd and alkyd emulsion coatings.

Conventional Solid Resins

- Can boost drying performance, particularly used to reduce cobalt levels or eliminate cobalt by use in conjunction with less active primary driers
- Reduce of loss of dry effects caused by pigment adsorption of driers

Water Based

- Boost drying performance
- Reduce hydrolysis of metals thus reducing or eliminating loss of dry problems

High Solids Coatings

- Reduced drying times
- Can prevent wrinkling in thicker films
- Reduced yellowing

Negative Effects

- Aromatic amines are toxic
- Non-aromatic amines have a lower activity so a higher loading is required
- Amines generally increase the yellowing of the film

Loss of Dry

Loss of dry is often observed in highly pigmented systems, particularly those pigmented with carbon black, toluidine blue, green and red and other such pigments. Although not as common, this phenomenon can also be observed in whites and pastels. Loss of dry occurs by irreversible absorption of the active metal driers onto the surface of the pigment, rendering the metal driers inactive for curing of the coating. This phenomenon is typically observed over time and is manifested by a longer cure or dry time with aging of the coating.

Loss of Dry Additives – Feeder Driers

- Replenish active metals adsorbed onto pigments (dark colors)
- Release additional metals in controlled manner
- React slowly with residual resin acidity
 - Durastab[®] LF
 - Duroct[®] Cobalt 21%

Loss of Dry Additives – Sacrificial Driers

Calcium can be used as a sacrificial agent. The Calcium is absorbed or interacts with the material causing loss of dry. This reduces the interaction of the active driers and thus reduces the loss of dry. The earlier the Calcium is added to a formulation the greater this effect will be.



Drier Dosage

General starting point recommendations for individual metals and blends can be provided. The recommendatiosn for a coating based on standard long oil alkyd will differ from that for a short oil alkyd or a high solids coating; similarly the nature of the oil / fatty acid and any hybridisations will change the optimal drier package. The Dura driers for water borne alkyd based coatings are designed for ease of use, and the type of technology will determine the optimal drier package.

In order to attain maximum performance of a coating the formulator needs to find the right balance of primary, through, auxiliary driers and additives. Specific metals can provide the means for a coating to improve defined qualities; such as increased hardness, higher gloss, better through dry.



Drier Trouble-shooter

Tech Brief – Drier for Coatings Troubles