EGEDRY® PRIME

Your Solution to the Cobalt Restriction

Technical Document

EGE KİMYA TECHNICAL TEAM

EGE KİMYA

Principals of paint drying process

Oil based paint is among the oldest coating technology in the world. Manufactured departing from bio-renewable raw materials like fatty acids from plants, alkyd resins offer some unique performance characteristics that petroleum based counterparts cannot compete with. One can cite abrasion resistance, high gloss and chemical resistance among these characteristics. “Drying”, a misnomer that industry has long been using instead of “curing”, relies on oxygen from the ambient and metal carboxylates that initiate and sustain free radical formation within the system that results in cross-linking of the paint binder.

Lead was the metal of choice for centuries considering the ultimate film properties of the coatings. When the health related risks of this metal became obvious, other metals were combined to replace its function.

Figure 1. "Mona Lisa" by Leonardo da Vinci. Oil on canvas (1503).

Cobalt Octoate: “the primary drier”

Bivalent cobalt undergoes a redox cycle that generates the exact needed energy to initiate the free radical formation from peroxides formed by absorbtion of ambient oxygen. The bivalent cobalt ion is introduced in the coating formulations most commonly in the form of a fatty acid ester: cobalt bis 2-ethyl hexanoate, or more popularly known as “cobalt octoate”. Combined with other metal carboxylates such as calcium, zirconium, strontium octoate, etc. an ideal curing, or “drying” is obtained.

Figure 2. A painter watching the paint dry.

Cobalt Octoate: health risks

The very property of cobalt octoate that gives its function as a curing agent raised questions about its safety on human health and environment. The redox cycle it undergoes makes it basically a reactive oxygen species (ROS) generator that is responsible for DNA damage and cell death. The real trouble is, any catalyst that will catalyse the curing of unsaturated organic system in presence of oxygen has to be a ROS promoter by definition. This means that any different metal or a metal combination, or other ligands most probably will not be a safe replacement for this popular drier.

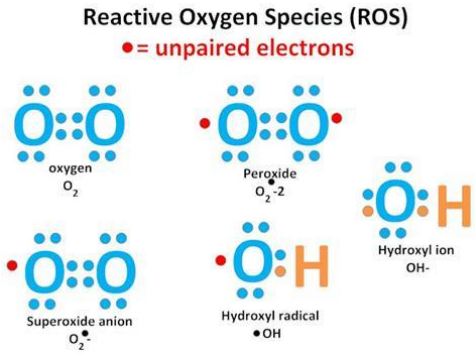


Figure 3. Reactive Oxygen Species (ROS). Photo credit: Joyce E.M. Wall (original artwork; Copyright ©2009 Joyce E.M. Wall)

Figure 4. Reactive oxygen species, in the form of ions, free radicals, or peroxide, can alter or damage many targets within cells. These targets include, clockwise from the top: iron-sulfur clusters; sulfhydryl groups; proteins; lipids; and DNA. Image courtesy of Edith Butler Gralla. http://www.pnas.org/content/105/24.cover-expansion.

The health concerns on cobalt octoate could result in some restrictions of its usage in coatings. To date, there are no official claims as to if and when this material will be restricted or banned from coatings formulations. Paint manufacturers, especially those that are active in the EU have already started to think about viable alternatives.

EGEDry® Prime: “the safe primary drier”

EGE Kimya who has manufactured metal carboxylates for over fourty years has concentrated its R&D efforts to come up with a product that will be as effective as cobalt octoate, but that will not share the same level of health concerns. The solution was EGEDry® Prime.

EGEDry® Prime is a cobalt carboxylate offered in a polymeric form. The polymeric structure decreases the water solubility of cobalt ion significantly, while maintaining all other performance characteristics unchallenged.

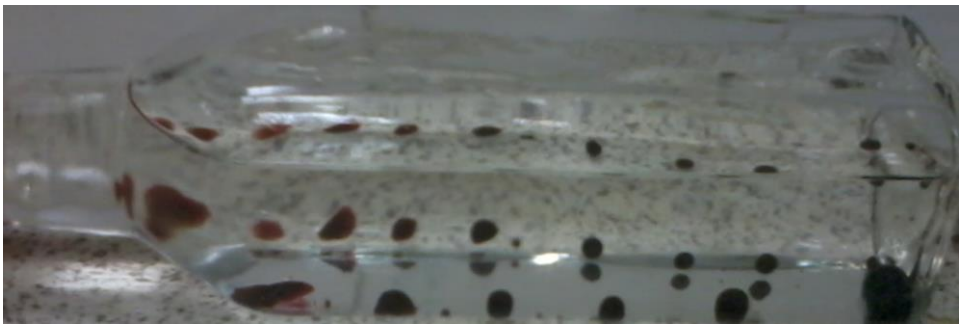
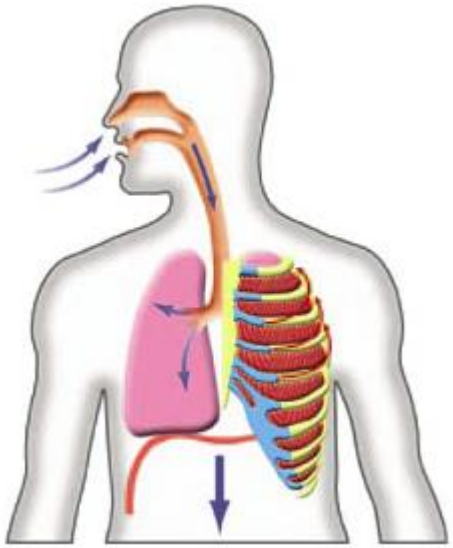


Figure 5. EGEDry® Prime's low water solubility causes bead formation when mixed in water.

EGEDry® Prime’s low bioavailability

Due to low watersolubility, EGEDry® Prime’s bioavailability is very low. Water solubility tests carried out in synthetic lung fluid according OECD 105 guideline for this type of test have revealed that cobalt ions do not tend to transfer to the aquatic media from EGEDry® Prime. Due to this fact, living cells stay protected from possible harms of ROS generated by cobalt ions.



To further prove the effect of low bioavailability, mutagenecity and genotoxicity tests are carried out on EGEDry® Prime. Based on DNA damage tests using in-vitro alkaline comet assay in the presence and abscence of metabolic activation, EGEDry® Prime proved to be non-genotoxic. Bacterial reverse mutation (Ames) test according to OECD guidelines (471), EGEDry® Prime is declared non mutagenic. These results come as no surprise, since this product’s bioavailability is very low.

EGEDry® Prime's REACh status

REACh regulation (EC 1907/2006) states on Article 2 (9) that "The provisions of Titles II and VI shall not apply to polymers." Title II deals with registration and Title VI concerns evaluation of substances. Since EGEDry® Prime is a polymer, it stays out of REACh's scope.

This status might change in the near future and polymers could partly be included in REACh system. In this scenario EGE Kimya is already prepared for a possible change of scope that could include polymers in REACh regulation.

EGEDry® Prime's CLP status

A polymer is a substance and must be notified on the basis of Article 39(b) and 40(1) of the CLP Regulation (EC 1272:2008) if it fulfils the criteria for classification as hazardous and it is placed on the market. Toxicological tests carried out in international laboratories have not shown any hazards of EGEDry® Prime. Accordingly, EGEDry® Prime does not have to be declared on the product's label.

EGEDry® Prime's performance

With all the benefits of reduced health and environment risks, EGEDry® Prime still performs at the level of traditional cobalt octoates. Tests carried out on long and medium oil alkyd resins proved that there is no pronounced difference between a traditional cobalt octoate and EGEDry® Prime, when formulated in the same metal-to-resin ratio.

The good news is that replacing a traditional cobalt octoate with EGEDry® Primes does not require a reformulation. Since the good old cobalt does the job, drying time, final film properties, tint and color do not change. It is true that EGEDry® Prime is a polymer and has a higher viscosity compared to traditional cobalt driers. However, this does not become an issue in mixing in this new drier into the paint formuation. All of our drying tests are carried out without any aging after mixing. Some of our customers who prefer to run drying tests as a QC measure before unloading a batch found this very relieving.

It goes without saying that every formulation has to be tested for performance before replacing the old cobalt driers. It is most probable that EGEDry® Prime will deliver the expected performance.

In the following graphs, you will see a comparison of EGEDry® Prime to cobalt bis(2-ethyl hexanoate), commonly refered as "cobalt octoate".

Table 1. Alkyd paint formulation for performance testing.

Standard Long oil alkyd (70% solid content)
Standard mix; Co-Ca-Zr (metal contents are fixed) Cobalt: 0,013% Calcium: 0,06% Zirconium:n0,06%
Solid content of paint formulation 65%
pVc = 18%
HSD; 23 m/se c, 30 min dispersion
Test conditions: 25 ºC and 55% relative humidity

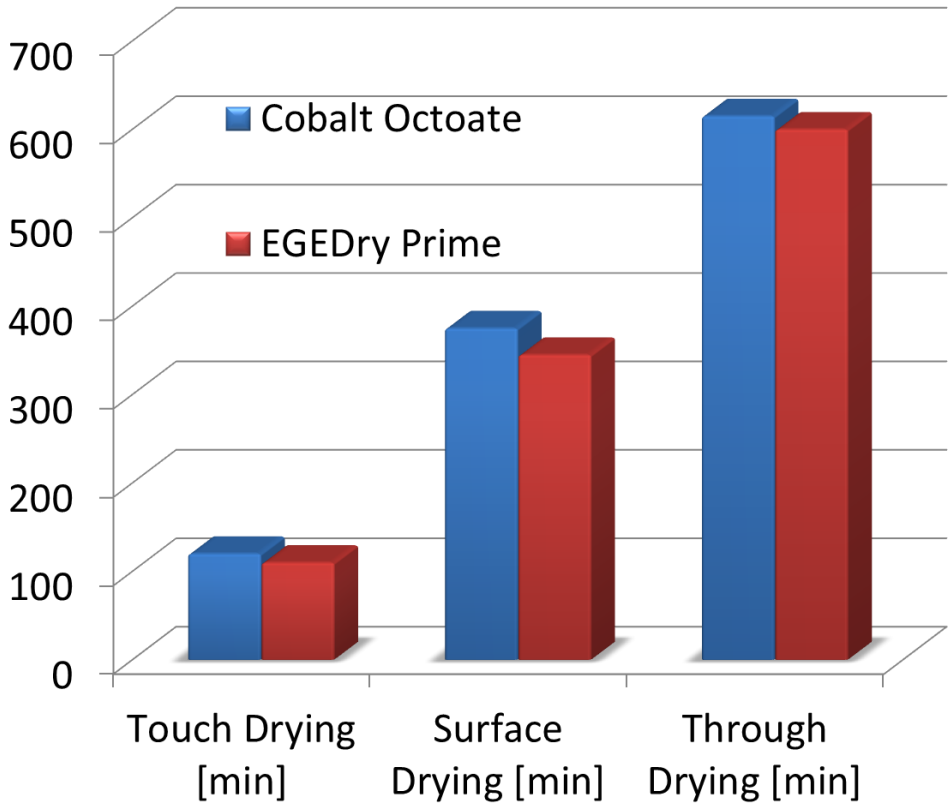


Figure 6. Drying time comparison of long-oil alkyd resin formulated with EGEDry® Prime and Cobalt Octoate

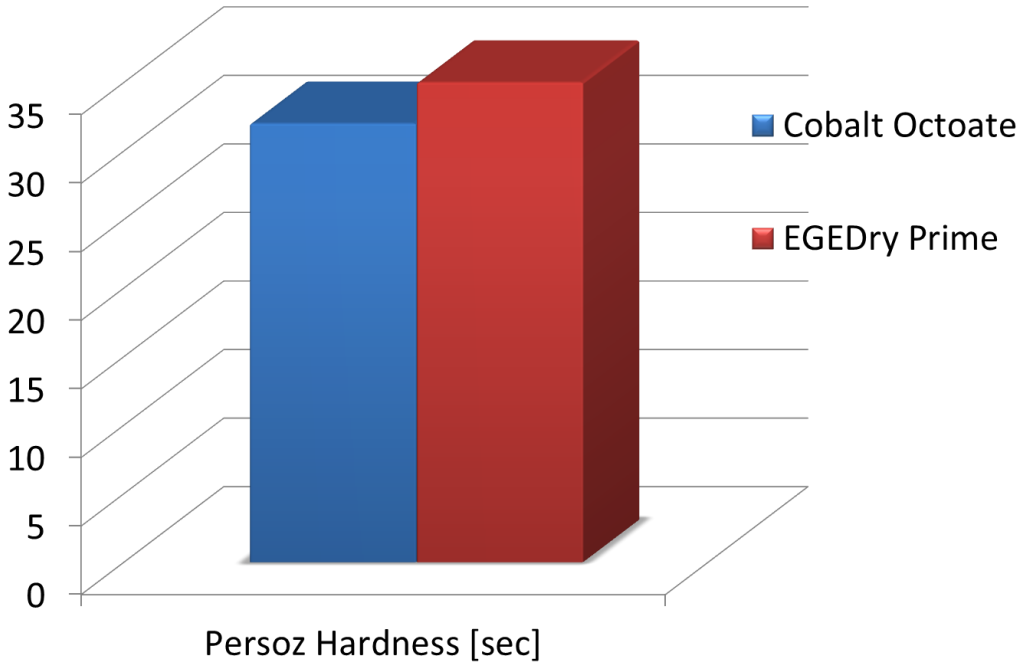


Figure 7. Persoz hardness comparison on paint formulated with EGEDry® Prime vs. Cobalt Octoate. 120 µm wet film application (45 µm dry film) on glass panels. Tested one week after application.

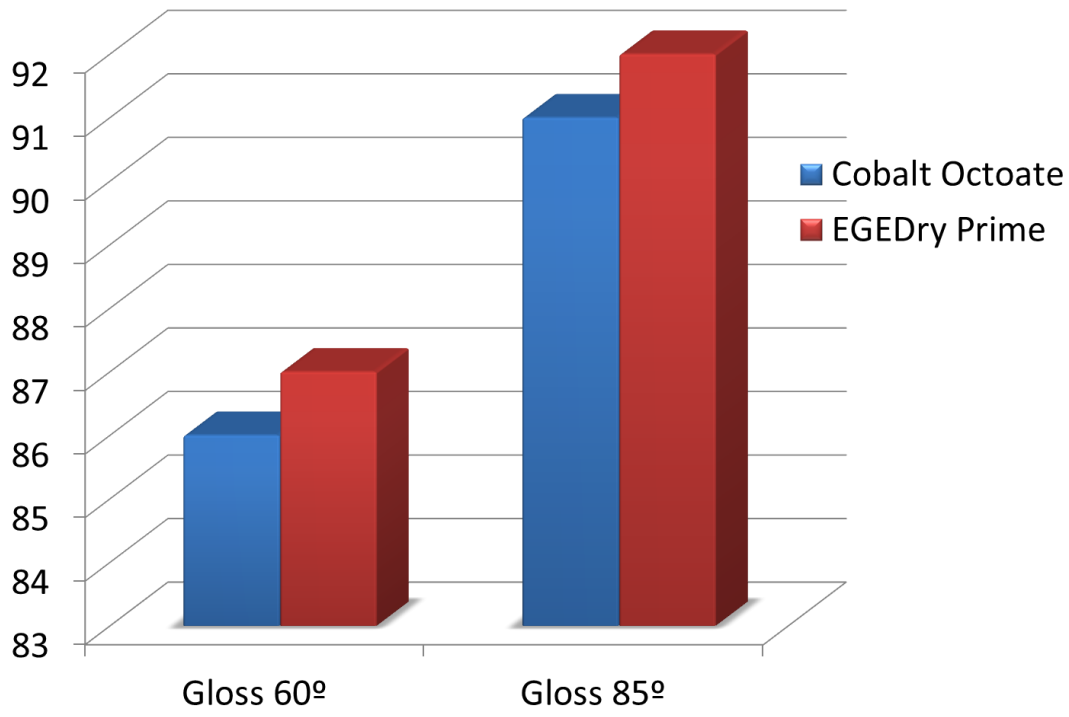


Figure 8. Gloss comparison on paint films formulated with EGEDry® Prime and Cobalt Octoate. 120 µm wet film application (45 µm dry film) on lenata cards. Tested one day after application.

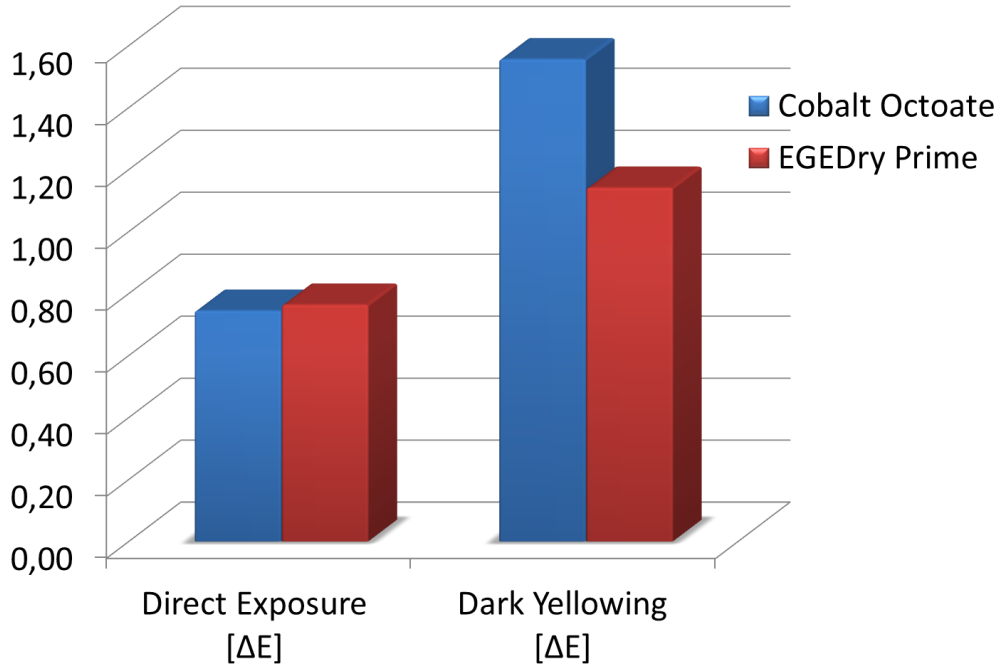


Figure 9. Yellowing in dark conditions and under direct sun light exposure on paint films formulated with EGEDry® Prime and Cobalt Octoate. ΔE calculated based on L*a*b values measured after 1 day and after 3 months. Direct exposure under sunlight (June, July, August). Wrapped in aluminum foil for dark yellowing test.

Storing EGEDry® Prime

Being an oxidative catalyst and a polymer at the same time, EGEDry® Prime runs the risk of "self-curing" if provided with enough oxygen and temperature. This means that if a package is opened and is not consumed within a couple of weeks, there might be some skin formation on the surface of the product. Although this is not the ideal situation, this will not affect the rest of the product. Best practice is to buy EGEDry® Prime in small enough quantities that opened emballages will not be exposed to oxygen for long, or, if one has the means, an inert nitrogen blanket could prevent this adverse effect.

EGEDry® Prime is a proprietary technology of EGE Kimya A.S.

EGEDry® Prime is a proprietary technology developed by EGE Kimya:

> Our international application under No. WO 2014/137307 has been published on 12 September 2014 and it will enter national phase in the designated offices by 06.09.2015

EGEDry® Prime is currently sold in industrial scale

Frequently Asked Questions

1. Addition of EGEDry Prime to paint formulations:

a. Mixing speed? - *Lab tests have not revealed any difference but since the viscosity is higher than traditional driers, a longer mix time could be needed.*

b. Mixing sequence? - *No change needed.*

c. Additional protective equipment? - *No.*

2. Dosage in the formulation:

a. Should the metal dose be calculated based on binding solids or the total formulation material? - *Binding solids.*

b. What is the ideal amount needed? - *0.05 PHR cobalt metal is the starting value for alkyd paints and varnishes. This translates to 1.25 PHR EGEDry® Prime.*

c. What should be the ratio of other driers? - *Same as what is used with a traditional cobalt drier.*

d. What are the probable changes with different types of alkyds? - *Based on lab results, it is highly expected that EGEDry® Prime will behave very similar to traditional cobalt driers.*

e. Any changes based on different oil lengths? - *Not expected.*

3. Possible changes in the final product:

a. Any probable reaction with other possible ingredients in the formulation? - *None was observed during lab trials so far.*

b. Any differences in the appearance of final product? - *No and this is the major advantage of EGEDry® Prime over replacing cobalt driers with other metal formulations.*

c. Changes in drying speed ? - *So far all of the drying test comparisons with traditional driers gave similar results.*

4. Changes on the dry film:

a. Any affects on the film surface? Does it affect spreading? - *No.*

b. Effect on the film color (difference in L,a,b values)? - *Same as traditional cobalt driers.*

c. Any differences in the film applied after ageing?

i. Problems in spreading? - *No.*

ii. Changes in film color (difference in L,a,b values)? - *No.*

d. Differences in dL, da and db values after exposure to UV light? *– Based on introductory results, EGEDry® Prime gives comparable yellowing values compared to traditional cobalt – based driers.*

e. Differences in dL, da and db after dark yellowing? *- Based on introductory results, EGEDry® Prime gives lower yellowing values compared to traditional cobalt – based driers.*

5. Differences on wet paint?

a. Any differences in viscosity and / or rheology? *- No.*

b. Any differences in the paint container's appearance? *- No.*

c. Any difference in viscosity increase during storage? *- Not different than traditional cobalt driers.*

6. Health and Regulatory

a. When will cobalt be restricted from paint formulations, would it be logic to use a drier that contains cobalt? *– This is the most wide misunderstanding of the issue: it is not cobalt, but cobalt compounds that are investigated separately for possible health risks. Some cobalt compounds like cobalt acetate and cobalt sulfate are already classified group 2B carcinogens. On the other hand, cobalt is also added in form of vitamin B12 to animal feed. In fact, vitamin B12 defficiency in humans could cause irreversible damage to brain and nervous system. The compounds currently under risk of restriction in coatings industry are cobalt neodecanoate and cobalt bis 2-ethylhexanoate.*

b. Although EGEDry® Prime is non-mutagenic and nongenotoxic, would the cobalt in the dry paint be a health risk for end users? *– Detailed scientific investigations have revealed that there is a negligible amount of bioavailable cobalt in dust sanded off from dried paints. Just like EGEDry® Prime, cobalt in dry paint will not have carcinogenic risks on living organisms.*

c. As much as EGEDry® Prime's safety is proved in the lab tests, wouldn't it be safer to use an oxidative drier that is "cobalt-free"? *– Manufacturers of new products have to release their toxicological data. Any oxidative drier that could replace cobalt octoate in performance, will most probably replace it in toxicological effects if it is bioavailable.*