REACH decisions on Cobalt have an impact on North America. Alternatives are present today that will ease future transitions.

Anthony Bennett
Technical Development Manager – Thermoset products Americas
AkzoNobel Functional Chemicals

Cobalt is a main component of unsaturated polyester resin systems. In these resins, cobalt metal salts are added to expedite the decomposition of organic peroxides at ambient temperature. Cobalt has been designed into resin formulations throughout many ambient and some higher temperature applications as it was readily available and fairly inexpensive. So what will happen when users of polyester materials cannot use cobalt any longer? That day could be soon in Europe and possibly the rest of the world soon after. The expectation for cobalt materials to be listed as carcinogens is real. What alternatives will be forced on the unsaturated polyester industry to continue to make composite products?

Today's story really starts with REACH, the European Community Regulation on chemicals and their safe use (EC 1907/2006). REACH deals with the Registration, Evaluation, Authorization and Restriction of Chemical substances. The self described program of REACH is to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. At the same time, REACH aims to enhance innovation and competitiveness of the EU chemicals industry. So we understand now that the purpose of REACH is to reduce the number of hazardous chemicals or better contain those chemicals for the benefit of the community. Many chemicals have already been regulated and now some of the focus is on cobalt and many cobalt derivatives.

Cobalt is the chemical element with symbol Co and atomic number 27. It is found naturally only in chemically combined form. The free element, produced by reductive smelting, is a hard, lustrous, silver-gray metal. Several cobalt compounds are used in chemical reactions as oxidation catalysts. Cobalt acetate is used for the conversion of xylene to terephthalic acid, the precursor to the bulk polymer polyethylene terephthalate. Typical oxidation catalysts are the cobalt carboxylates (sometimes referred to as cobalt soaps). They are also used in paints, varnishes, and inks as "drying agents" through the oxidation of drying oils. When cobalt carboxylates are used in polyester resins they are known as promoters or accelerators, initiating gel and cure in combination with organic peroxide initiators. Cobalt Naphthenate, Cobalt Octoate (also known as cobalt bis(2-ethylhexanoate)), Cobalt Decanoate and Cobalt Neodecanoate are common products in unsaturated polyester resins and coatings. The percentages of cobalt metal in these compounds vary.

Globally, cobalt and many of its derivatives are listed as poison but cobalt metal also is an essential element for life in minute amounts. The median lethal dose LD50 value for soluble cobalt salts has been estimated to be between 150 and 500mg/kg. Thus, for a 100kg person the LD50 would be about 20grams. After nickel and chromium, cobalt metal is a major cause of contact dermatitis and is being considered as possibly carcinogenic. In 1966, the addition of cobalt compounds to stabilize beer foam in Canada led to cardiomyopathy, which came to be known as beer drinker's cardiomyopathy.

Under REACH legislation, cobalt carboxylates like cobalt bis(2-ethylhexanoate) were placed in evaluation by the European Chemical Agency (ECHA). In August 2012, cobalt bis(2-ethylhexanoate) was classified as CMR2 Reprotoxic. CMR stands for carcinogenic, mutagenic and reprotoxic (toxic to reproduction). This classification was done through CLP regulation on the classification, labeling and packaging of substances and mixtures by the Cobalt REACH Consortium, a group of producers and users of cobalt products. The Cobalt REACH Consortium continues to provide research information to ECHA for REACH. It is possible that the research data could lead to a further cobalt carboxylate reclassification as CMR Carcinogenic 1b . Already in Europe, some inorganic cobalt salts such as cobalt sulfate were classified as lung carcinogenic CMR 1b, reproductive toxin category 1B and mutagenic category 2. With this classification, each manufacturer is obligated to demonstrate the safe and healthy use of these cobalt containing products. A CMR Carcinogenic 1b reclassification of cobalt carboxylates will be a great challenge to all users. The effect of such legislation would restrict the use of cobalt carboxylates in manufacturing composites. There is some debate that resins containing more than 0.01% cobalt metal would have to be labeled CMR Carcinogenic 1b. The unsaturated polyester resin industry then is affected due to the extensive use of cobalt carboxylates in the many fined-tuned formulations that exist.

You might ask how the actions of the European community can have an effect on the composite industry in the Americas? Simply, there are global implications when regulatory changes in any region occur. There is the need for globally oriented companies to adapt to these new needs. So, there are new developments that exclude the “offensive” materials and opportunity to build around new products. Those companies that find success in new technology, driving other companies that are possibly not as global to also change. Older more “offensive” products are soon discontinued in favor of the new technology.

Cobalt-free accelerators

Anticipating increasing environmental pressure on cobalt, some companies are leading the way with a range of cobalt-free accelerators. Much of the new technology is versatile and delivers acceleration in many applications that formerly required cobalt.

The new cobalt-free accelerators are based on copper, manganese and iron and can be used as alternatives for conventional cobalt-based accelerators. They are pre-formulated, are easy to use, and can be mixed at room temperature into a standard polyester base resin which makes them suitable for all composite component manufacturers, end-users and resin manufacturers. Pre-accelerated resins with this new technology will work with organic peroxides to cure to the same standards currently in place.

General descriptions based on tests conducted in five commonly used resins and four standard curing organic peroxide systems are shown in Figure 1. The resins tested were a high reactive orthophthalic resin, a medium reactive orthophthalic resin, an isophthalic resin, an epoxy based vinyl ester resin, and a dicyclopentadiene (DCPD) resin. The curing systems tested were a methyl ethyl ketone peroxide (MEKP-1), an acetyl acetone peroxide (AAP), a ‘low hydrogen peroxide, high dimer content MEKP peroxide (MEKP-2), and a cumyl hydroperoxide (CHP).

The accelerators were tested for gel time, time-to-peak exotherm and peak exotherm. The tests included standard Society of Plastics Industry (SPI) ASTM D7029 or ISO 84 normalized testing using 50% quartz sand filler and 0.15 inch (4 mm) laminates with 30% glass reinforcement. All tests were done at 68ºF (20°C) and at elevated temperature 176ºF (80°C). The effort was to reproduce results at ambient conditions and temperatures that mimic applications for artificial stone and panels.

The performance in laminate curing was monitored by Barcol hardness development.

Figure 2 depicts the test results for two copper-based accelerators (Cu-1 and Cu-2) in a medium reactive orthophthalic resin using MEKP. From the data shown it can be concluded that the reactivity of both cobalt-free accelerators is high and Barcol hardness development is fast while maintaining acceptable peak exotherm. The copper accelerators provide for faster processing and demolding. Gel times can be extended by using standard inhibitors like tert-butyl catechol (TBC) and butylated hydroxytoluene (BHT).

The test results demonstrate that the use of these cobalt-free accelerators lead to shorter cycle times and possibly lower residual styrene levels which equates to more thorough cure. The cobalt-free accelerators showed no gassing when used in combination with standard MEKP to cure an epoxy based vinyl ester resin at ambient temperature.

Cobalt-free acceleration in Resin Transfer Molding.

Even before the CMR2 reclassification of cobalt octoate, several companies had worked with cobalt-free accelerators. One company, NPSP Composieten BV using a copper-based accelerator, evaluated its use in resin transfer molding (RTM) production at ambient temperature. The evaluation was a straight forward process that demonstrated the flexibility and the mechanical properties of the end product are maintained.

NPSP Composieten BV now manufactures the composite Pastoe Low LC03 chair using copper based accelerator. The company is able to utilize a nature based composites label to show that the production methods used are both environmentally friendly and technically and economically feasible. NPSP Composieten BV has found that the mechanical properties of the chair are uncompromised and the finishing is excellent. The copper based accelerator was very comparable with cobalt-based accelerators in terms of variability of gel times, mechanical properties and visual properties.

Improving the curing process

The experience of NPSP Composieten BV shows how cobalt can be successfully replaced by a cobalt- free accelerator. Some cobalt-free accelerators are designed to combine high reactivity with process flexibility and secure the desired mechanical properties in the required product cycle time. It is also possible to improve the curing process by using a cobalt-free accelerator. Proper selection of cobalt-free accelerator and organic peroxide can have a positive impact on the residual styrene level.

Figure 1: Overview of available cobalt-free accelerators.		
Name	General description	Application area
Cu-1	Copper based	Cu-1 can be used for ambient temperature curing and shows excellent reactivity in most standard resins. It is successfully used in hand lay-up/spray-up applications and resin transfer molding (RTM).
Cu-2	Copper based	Cu-2 can be used for ambient temperature curing and shows excellent reactivity in most standard resins. It is successfully used in hand layup; spray up applications and in polymer concrete production. Curing performance in vinyl ester and dicyclopentadiene (DCPD) resins has been proven to be equal or better than cobalt. It has excellent shelf life stability and no gel time drift when used to pre-accelerate polyester resins. It is therefore particularly suitable for pre-accelerating resins which need a long storage time.
Mn	Manganese based	Mn shows good reactivity at elevated temperature curing (70-90°C). The main advantage of this product is that after curing it is nearly colorless.
Fe-1	Iron based	Fe-1 is specifically developed for elevated temperature curing of agglomerated stone slabs using a curing system based on such as tert-butyl peroxybenzoate, a peroxy ester. Some peroxy esters have been demonstrated to react at lower temperatures in resins containing cobalt. Fe-1 showed excellent curing with low residual styrene levels and the specific ability to reduce the activation temperature of peroxy esters,
Fe-2	Iron based mixed metal accelerator	Fe-2 has excellent curing performance at both ambient and elevated temperature and can be used with most standard polyester resins and curing systems.
Fe-3	Iron based mixed metal accelerator	Fe-3 can be used for ambient temperature curing and shows excellent curing in most standard polyester resins with a specific advantage of low residual styrene levels when used in an Isophthalic or DCPD resin systems.

Figure 2 Reactivity data for Cu-1 and Cu-2			
Amount (pph)			
Medium reactive ortho resin	100	100	100
MEKP	2	2	2
1% cobalt octoate solution	0.5		
Cu-1		0.7	
Cu-2			0.8
0.15 inch (4 mm) laminate at 68ºF (20°C)			
Gel time (min.)	19	32	29
Time to peak (min.)	46	57	54
Peak exotherm (ºF/°C)	100 / 38	117 / 47	129 / 55
Barcol hardness development			
After 3 hrs	20	38	50
After 6 hrs	34	40	51
After 24 hrs	45	47	52

The Pastoe Low Chair 03 (designed by Maarten Van Severen and Fabian Schwaerzler for Pastoe) is manufactured by NPSP Composieten BV using cobalt-free accelerator.

AkzoNobel has developed several Nouryact™ accelerators that are 100% cobalt-free and allow for the use of the BluCure™ seal. The BluCure Seal is a guarantee that products are cured with 100% cobalt-free technology.

For further information go to www.akzonobel.com/polymer, www.nouryact.com, and www.blucure.com

Further information
Anthony Bennett, Technical Development Manager
Thermoset Products Americas
AkzoNobel Polymer Chemicals, LLC
12900 Bay Park Road
Pasadena, TX 77573
USA
E-mail: anthony.bennett@akzonobel.com

Roel Zuijderduin, Technical Development Manager
Thermoset Products Europe
AkzoNobel Functional Chemicals, Stationsstraat
77, P.O. Box 247, 3800 AE Amersfoort,
The Netherlands;
E-mail: roel.zuijderduin@akzonobel.com;
www.akzonobel.com/polymer

Willem Böttger, Director
NPSP Composieten BV, Küppersweg 31,
2031 EA Haarlem, the Netherlands;
E-mail: willem.bottger@npsp.nl;
www.npsp.nl

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AkzoNobel and DSM launch BluCure cobalt-free curing technology:
www.reinforcedplastics.com/view/24890/ akzonobel-and-dsm-launch-blucure-cobalt-freecuring-technology:
Cobalt-free curing taking off: *Reinforced Plastics edition January/February 2013, p. 29-32*
Cobalt-free curing based on Iron: *Reinforced Plastics edition march/April, p. 25-28*