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# A Study of Novel Alternatives to Cobalt Metal Complexes in Unsaturated Polyester Resin Systems



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International Exhibition and  
Congress on Composites,  
Polyurethane and  
Engineering Plastics

Expo Center Norte • Green Hall  
São Paulo – SP – Brazil

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# Metals in History of UPR

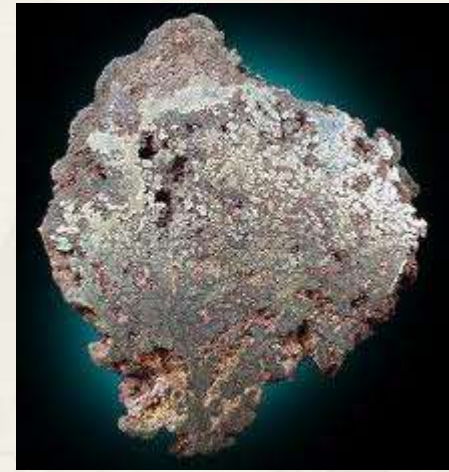
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## COBALT -Atomic number 27

- ❑ Georg Brandt isolated cobalt (Co) from metal 280 years ago
- ❑ Cobalt produced from smelting ore
- ❑ Cobalt “soaps” developed ~ 1900

# Metals in History of UPR

- Cobalt metal processed in several forms
  - Cobalt dichloride
  - Cobalt diacetate
  - Cobalt carbonate
  - Cobalt dinitrate
  - Cobalt sulfate
- Cobalt carboxylates (soaps) manufactured from cobalt dichloride or direct from metal



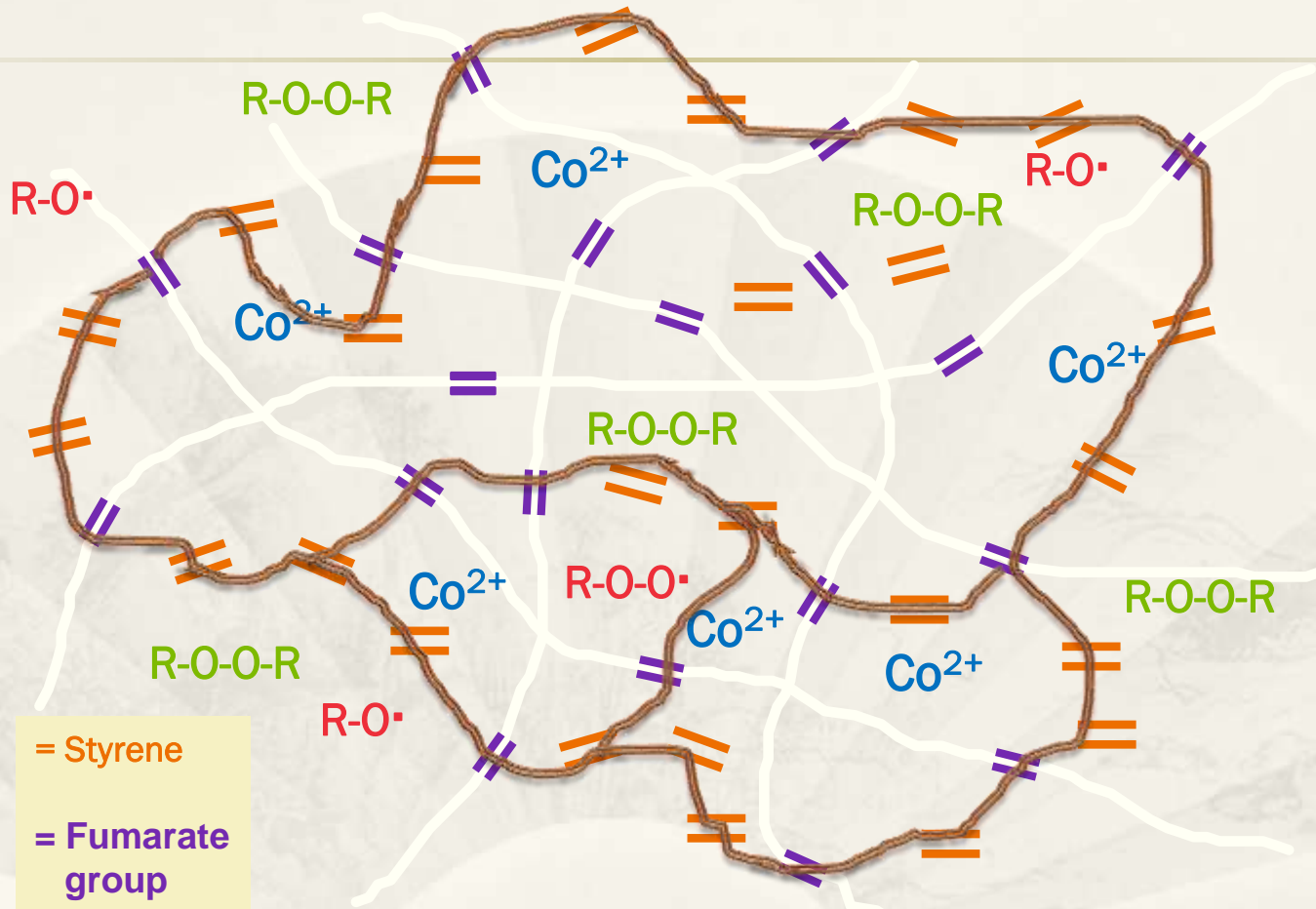
# Metals in History of UPR

- Cobalt carboxylates (cobalt soaps) are used in:
  - Paints
  - Varnishes
  - Inks (as "drying agents")
  - Polyester Resins (as gel and curing agents)





# The Structure of a Novel CR Resin

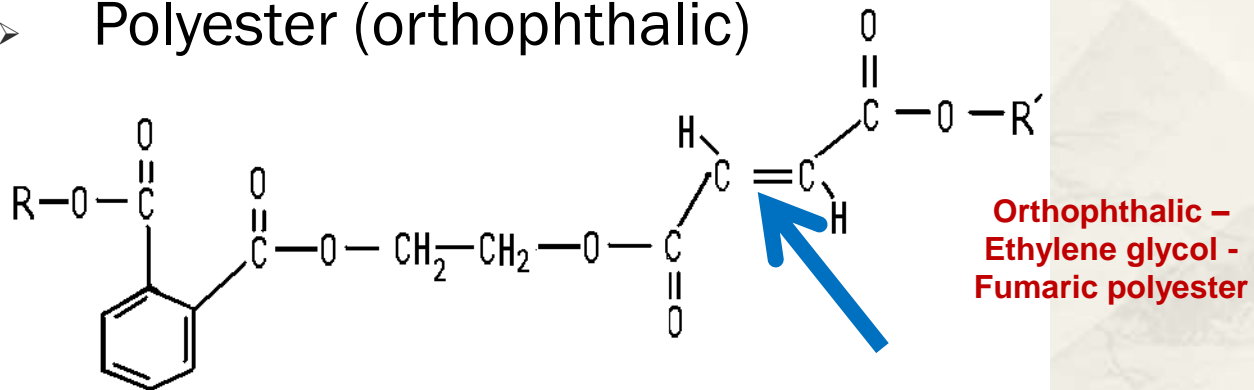


After Cure still some styrene and peroxide remain

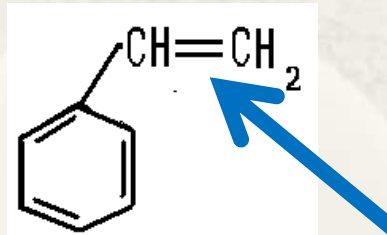
# Cobalt with Peroxides

- Where are the double bonds?

- Polyester (orthophthalic)



- Styrene (or other reactive monomer)





# REACH



# REACH Influences

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- ❑ European community regulation on chemicals and safe use
- ❑ Evaluate, register, authorize, restrict environmental hazard chemicals
- ❑ Enhance EU innovation and competitiveness
- ❑ **Progressive substitution of the most dangerous chemicals**

# REACH

- ❑ Why is Cobalt REACH Listed?
  - Just 20 grams is Lethal to a 220 lb person.
  - Cobalt can cause contact dermatitis
  - Cobalt maybe considered carcinogenic.
  - Identified as Substance of Very High Concern (SVHC)



# REACH

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- ❑ After SVHC
  - Goes to REACH Annex XIV
  - 3 years to “Sunset Date”
- ❑ No current date or deadline for REACH decision on cobalt

# Renewed Efforts and New Products

- ❑ Older Metal Compounds
  - Vanadium (V)
  - Manganese (Mn)
  - Calcium (Ca)
  - Zinc (Zn),
  - Tin (Sn)
  - Copper (Cu)
- ❑ Nickel (Ni) - Chromium (Cr) - Lead (Pb) have Toxicity issues



Not Cobalt Replacements



# Renewed Efforts and New Products

- New ligand chemistry developments

- Iron (Fe)

- Manganese (Mn)

- Titanium (Ti)

- Yttrium (Y)

- Strontium (Sr)

- Copper (Cu)

- Gadolinium (Gd)

- Neodymium (Nd)

- Gallium (Ga)

- Indium (In)

# Renewed Efforts and New Products

## Vanadium (a. n. 23)

| <b>Comparison of Vanadium to Cobalt accelerator complexes in Polyester Resin at 20°C (68°F)</b> |    |    |
|---|----|----|
| 1% Cobalt accelerator solution, phr   | 1  |    |
| 0.2 %Vanadium accelerator solution, phr   |    | 1  |
| Standard MEKP, phr  | 2  | 2  |
| Gel time, minutes   | 18 | 19 |
| Barcol Hardness, 934-1 gauge at 6 hours   | 0  | 37 |



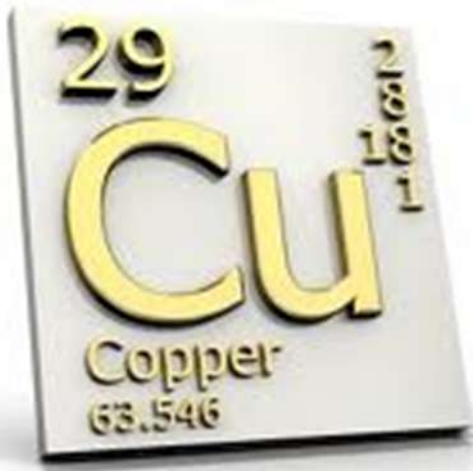
# Renewed Efforts and New Products

## Manganese (a. n. 25)

| <b>Cure Comparison of Manganese to Cobalt accelerator complexes<br/>in a Quartz Filled Isophthalic Polyester Resin at 20°C (68°F)</b> |          |          |
|---|----------|----------|
| 1% Cobalt accelerator solution, phr   | 1.0      |          |
| 0.5% Manganese accelerator solution, phr  |          | 1.5      |
| Standard MEKP, phr  | 1.5      | 1.5      |
| Gel time, minutes   | 9        | 9        |
| Peak Exotherm, °C (°F)  | 46 (115) | 61 (142) |
| Residual Styrene after 24 hours, %  | 2.4      | 2.1      |

# Renewed Efforts and New Products

## Copper (a. n. 29)



### Comparison of Copper (II) Acetate Accelerator complexes Polyester Resin at 20°C (68°F)

|                                       |          |          |
|---------------------------------------|----------|----------|
| Resin                                 | 1.0      |          |
| Accelerator                           |          | 1.5      |
| Resin                                 | 1.0      | 1.5      |
| Accelerator                           | 9        | 16       |
| Conversion, %                         | 55 (131) | 60 (140) |
| Residual Styrene after 24 hours, %    | 3.6      | 3.3      |
| Barcol Hardness, 934-1 gauge @ 1 hour | 10       | 45       |

\* 4 mm Laminate, 30% glass (chopped strand mat)

# Renewed Efforts and New Products

## Iron (a. n. 26)

| <b>Cure Comparison of Iron to Cobalt accelerator complexes in Orthophthalic Polyester Resin at 85°C (185°F)</b> |              |              |
|---|--------------|--------------|
| 6% Cobalt accelerator solution, phr   | 0.2          |              |
| Iron accelerator complex solution, phr  |              | 1.0          |
| Blend of tert-butyl peroxybenzoate and 2,4-pentanedione, phr  | 2.0          | 2.0          |
| Gel time, minutes   | 1.6          | 0.5          |
| Time to Peak Exotherm, minutes  | 5.9          | 5.3          |
| Peak Exotherm, °C (°F)  | 215<br>(419) | 214<br>(417) |

# Renewed Efforts and New Products

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## □ Other Complexes

- New technology in Lanthanides, Alkali and Transition Elements
- Toxicity and environmental impacts?

# Conclusions

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- ❑ Many cobalt compounds present health concerns (SVHC)
- ❑ Cobalt considered for Annex XIV?
- ❑ Va, Mn, Fe, Cu and other ligands now testing
- ❑ Many new cobalt replacements are commercialized.
  - Not listed with REACH

# Further Information

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The regulatory information was taken directly from the following websites:

## REACH:

- ❑ [ec.europa.eu/environment/chemicals/reach/](http://ec.europa.eu/environment/chemicals/reach/)
- ❑ [cobaltreachconsortium.org/GREEN](http://cobaltreachconsortium.org/GREEN)

ECHA : [echa.europa.eu](http://echa.europa.eu)

REVIEW THE REACH AND ECHA WEBSITES FOR  
INFORMATION FURTHER UPDATES

# References

- \* 1. Georg Brandt first showed cobalt to be a new metal in: G. Brandt (1735) "Dissertation de semimetallis" (Dissertation on semi-metals), Acta Literaria et Scientiarum Sveciae (Journal of Swedish literature and sciences), vol. 4, pages 1–10
- \* 2. Leo W.J. Damen, Salvatore Maira, "Accelerators for the Organic Peroxide Curing of Polyesters and Factors Influencing Their Behavior", presented at the 23rd Conference SPI Reinforced Plastics/Composites Division, Shoreham Hotel, Washington, D. C. February 6-9, 1968
- \* 3. Chemical & Metallurgical Engineering, Volume 22, January 7, 1922, edited by Eugene Franz Roeber, Howard Coon Parmelee, page 522
- \* 4. Plastics, 1960, Allan, L. H, page 250

# Appreciation



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