Scented Polyolefins from Ziegler-Natta Catalysts

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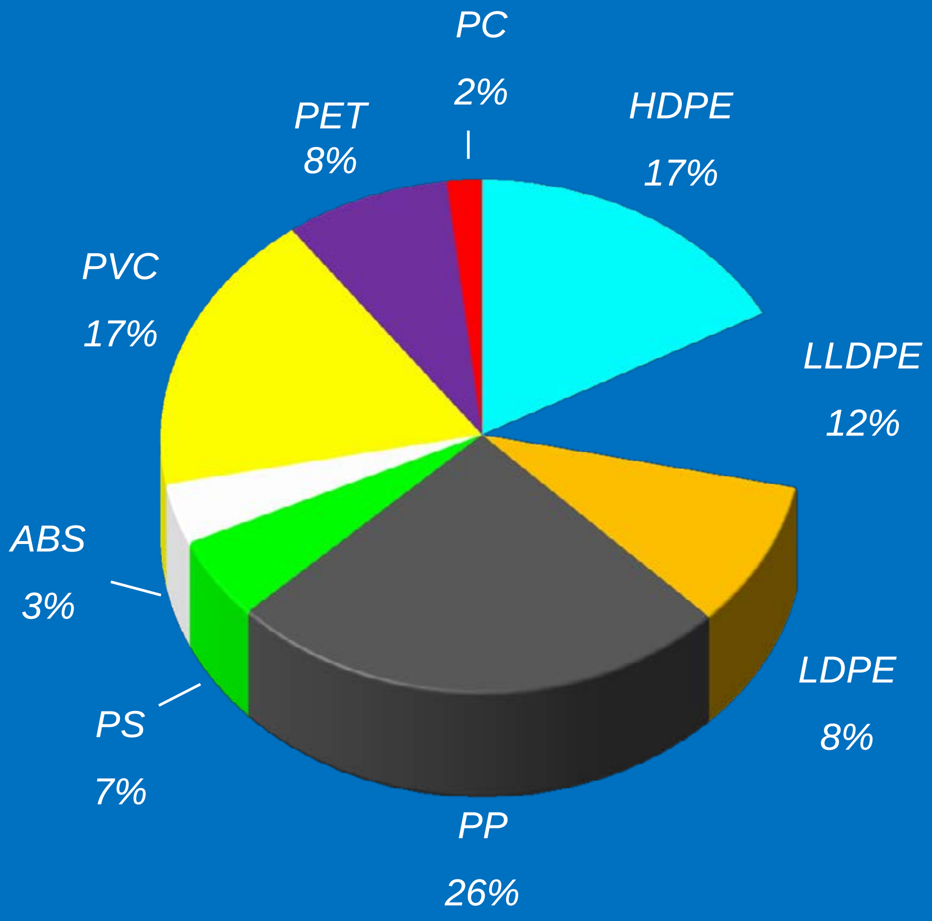
Introduction

Global Plastics Demand in 2015*



Total Demand:

240 million metric tons

(528 billion pounds)

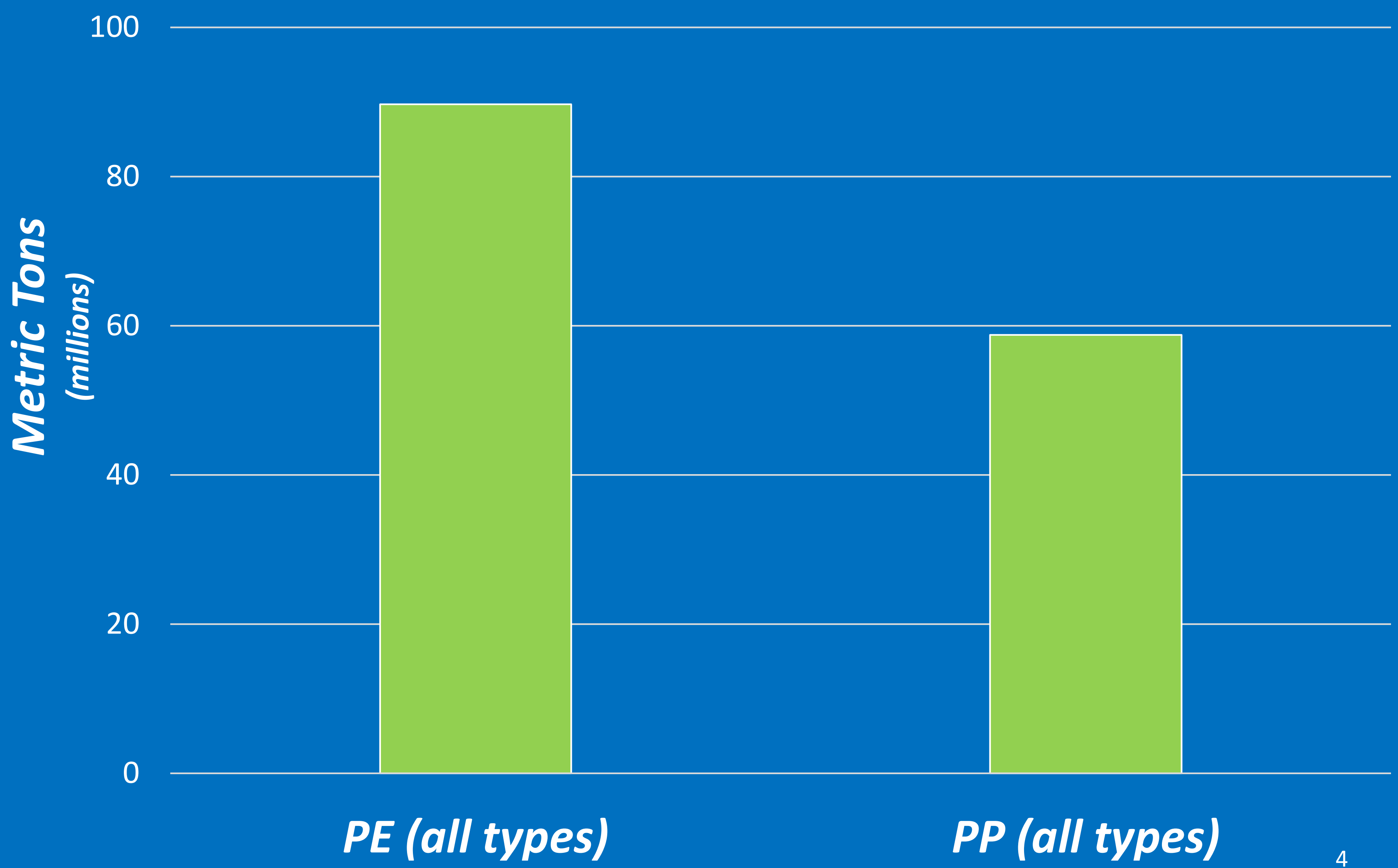
Total for Polyolefins:

151 million metric tons

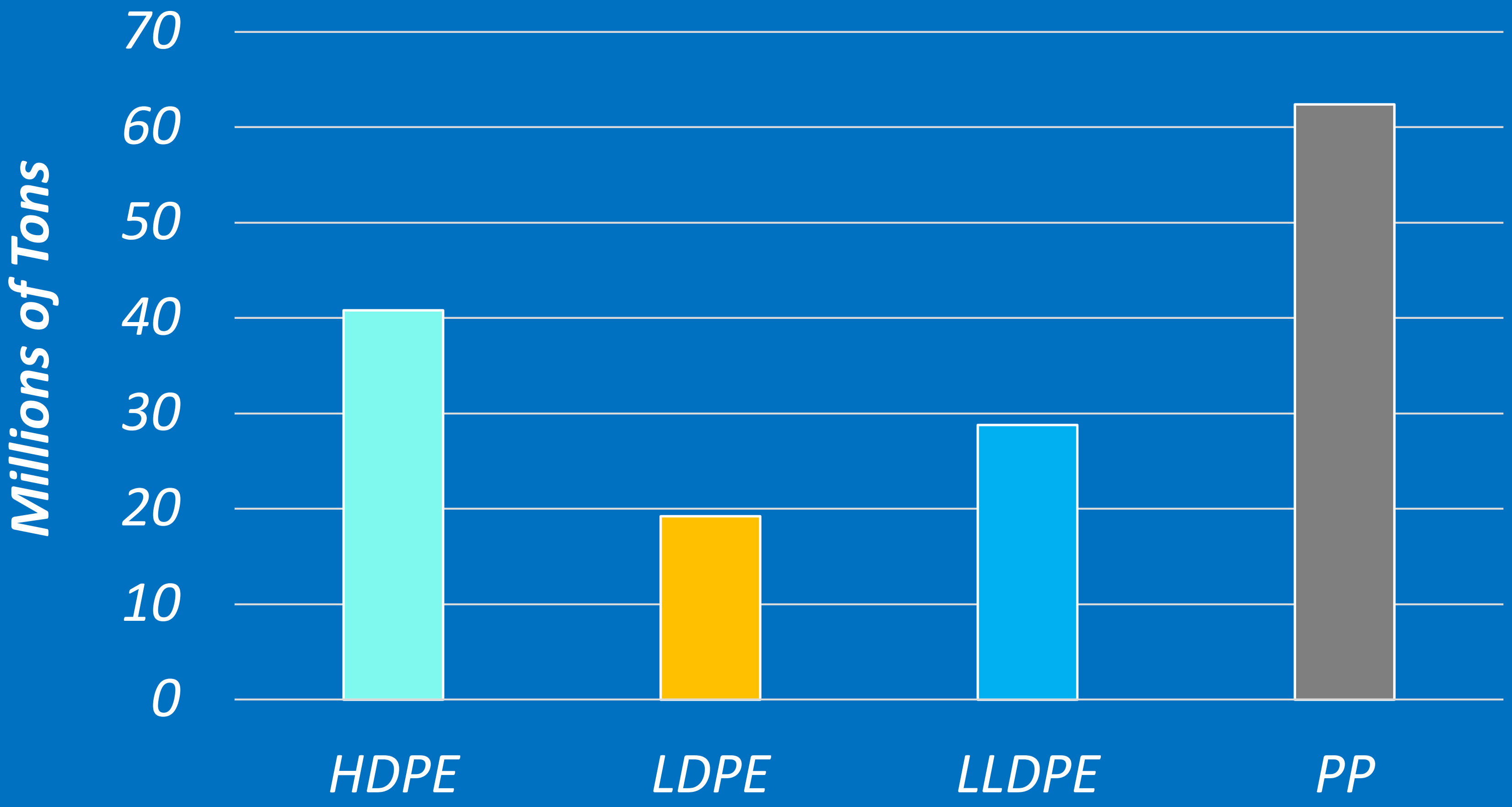
(333 billion pounds)

* H. Rappaport, IHS

Demand for Polyethylene and Polypropylene in 2015

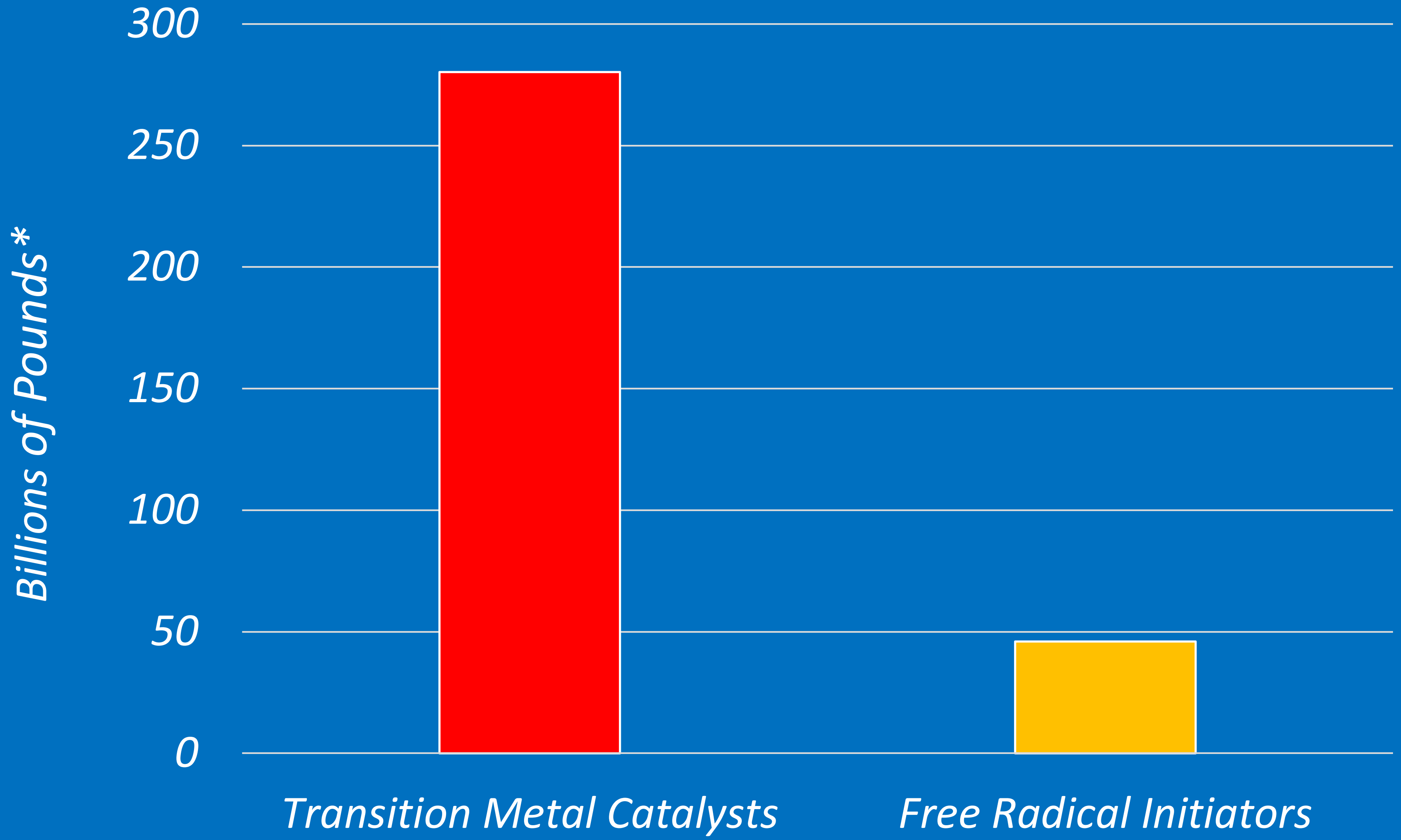


*Demand for Polyolefins in 2015**



** H. Rappaport, IHS*

How Are Those Billions of Pounds of Polyolefins Manufactured?



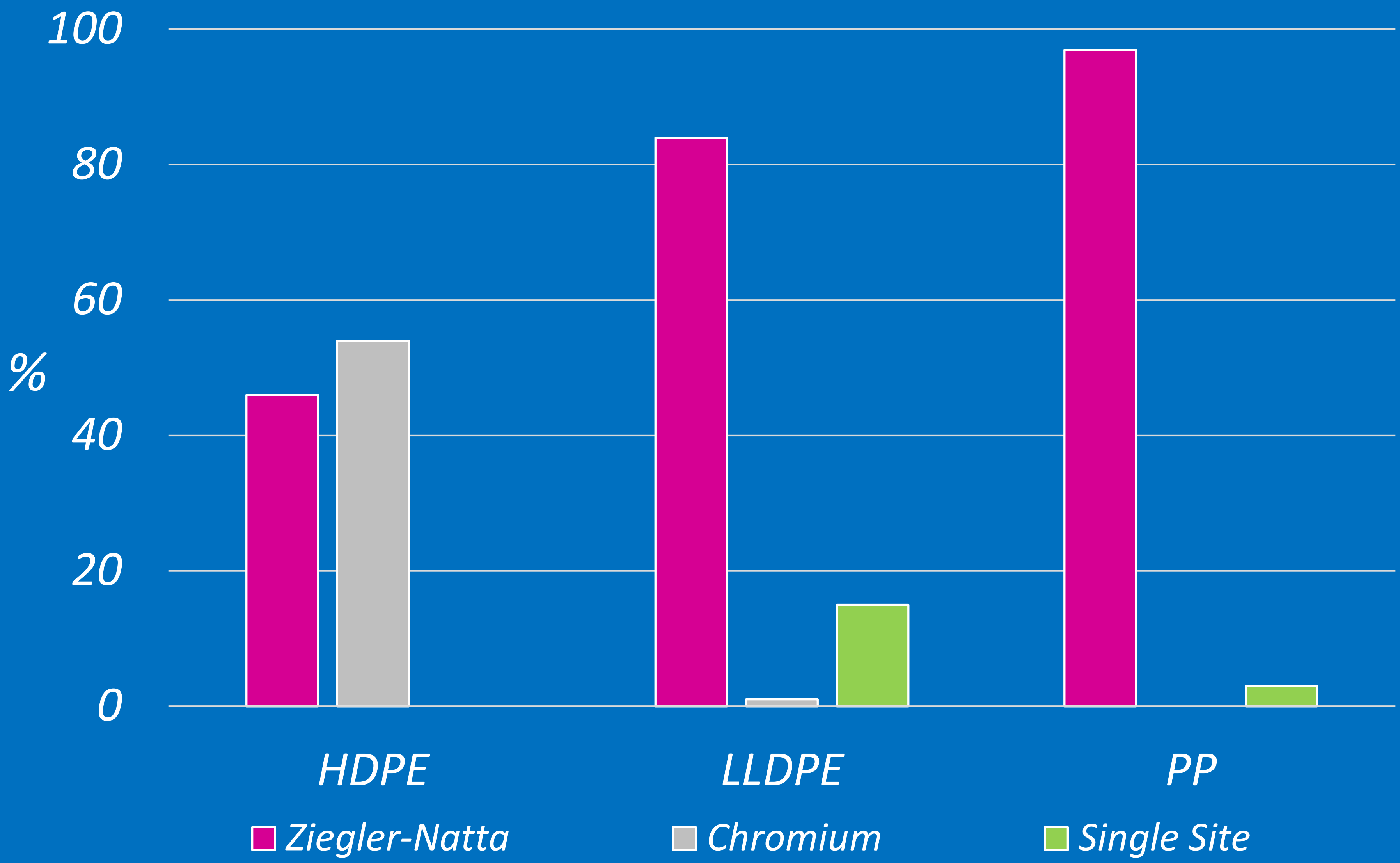
* Based on data provided by C. Lee, VP of Townsend Solutions

Initiators/Catalysts Used in Production of Polyolefins

- *LDPE* is produced with free radical initiators, mostly organic peroxides.*
- *All other polyolefins** are produced with transition metal catalysts:*
  - *Ziegler-Natta*
  - *Chromium (“Cr-on-silica,” “Phillips”, etc.)*
  - *Single-site (“metallocenes,” “controlled geometry,” etc.)*

** Includes EVA, EVOH, EMA, etc.*
*** HDPE, MDPE, HMW-HDPE, LLDPE, PP., etc.*

Transition Metal Catalysts in Production of Polyolefins*



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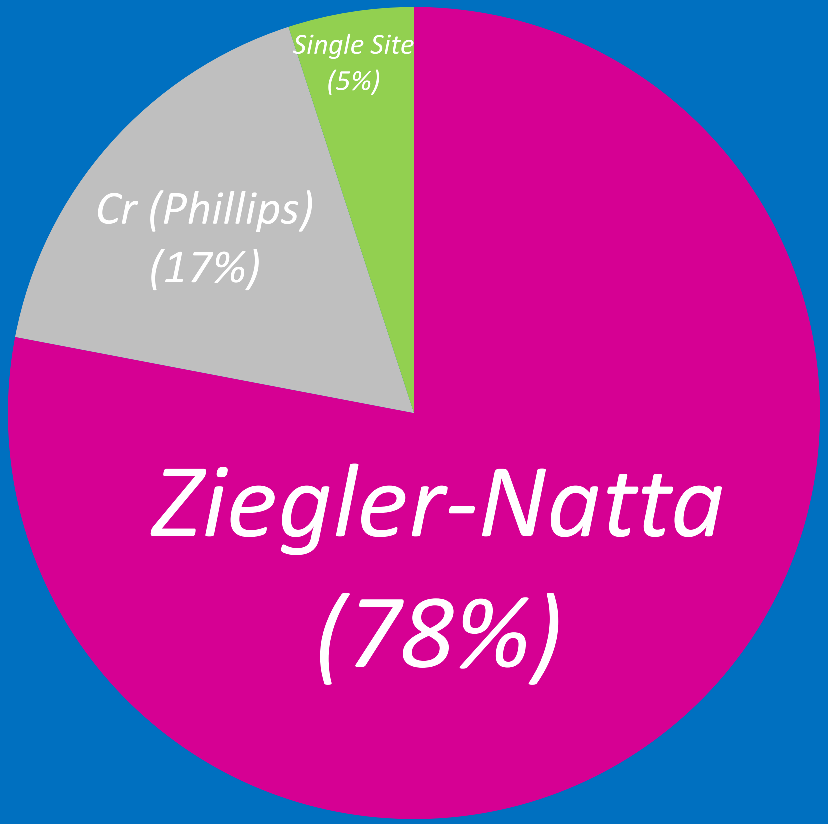
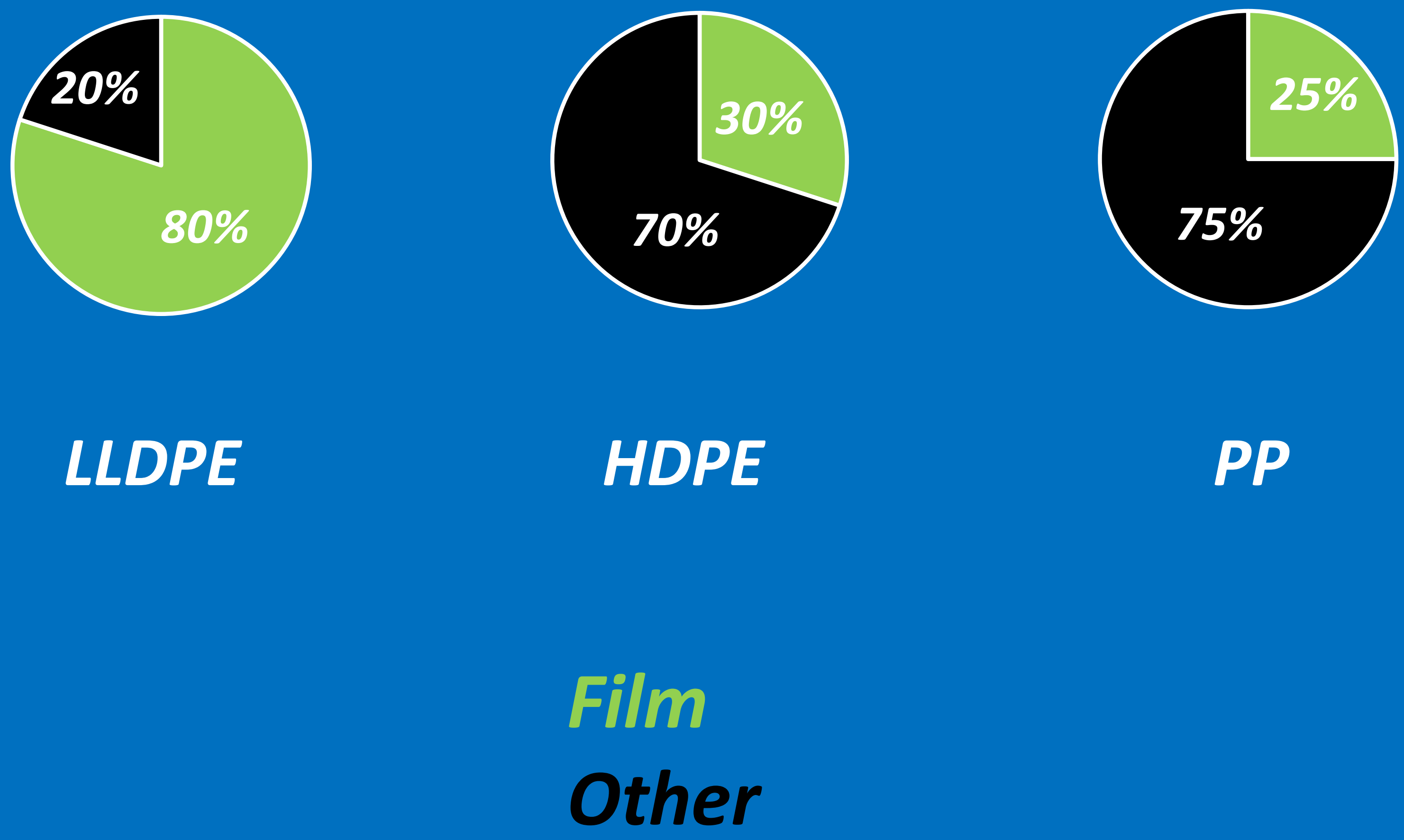
Transition Metal Catalysts in Production of Polyolefins*



* LLDPE, HDPE and PP. Based in part on data provided by C. Lee, VP of Townsend Solutions

Approximate Percentages of Polyolefins Used in Film Applications



Ziegler-Natta Catalysts

Ziegler-Natta Catalysts Defined

Transition Metal Compound + Metal Alkyl + Olefin → Polymer

"Catalyst" + "Cocatalyst" + Olefin → Polyolefin

"Ziegler-Natta Catalyst"

- *Named in honor of:*
  - *German chemist Karl Ziegler, who showed in 1953 that linear PE could be produced with transition metal compounds and aluminum alkyls, and*
  - *Italian chemist Giulio Natta, who expanded applicability to stereoregular (crystalline) polypropylene in 1954.*
- *ZN catalysts have been commercially available since 1960.*

ZN Catalysts

(cont'd)

Characteristics of ZN catalysts:

- *Complex solids, predominantly inorganic.*
- *Typically free-flowing powdery or granular solids with colors ranging from purple to gray to brown.*
- *Air- and moisture-sensitive (often smoke upon exposure). Must be handled under inert atmosphere.*

ZN Catalysts

(cont'd)

- *Titanium compounds are the most frequently used transition metal component. $TiCl_4$ is, by far, the most common.*

- *Industrial ZN catalysts have evolved from relatively inefficient, low-activity versions to remarkably high yield catalysts:*

  - *In early 1960s: 10^2-10^3 lb of polymer per lb of catalyst.*

  - *21st century: $\geq 10^4$ lb of polymer per lb of catalyst.*

- *Modern ZN catalysts are so active, it is no longer necessary to remove catalyst residues.*

Cocatalysts for Ziegler-Natta Catalysts

Cocatalysts for ZN Catalysts

- *The cocatalyst, sometimes called “activator,” is typically an aluminum alkyl. Triethylaluminum (TEAL) is the most common cocatalyst.*

- *Aluminum alkyls fulfill a variety of roles in Ziegler-Natta catalyst systems:*

  - *reducing agent for transition metal*

  - *alkylating agent to create active centers*

  - *scavenger of poisons*

Properties of Aluminum Alkyls

- *mostly clear, colorless liquids*
- *explosively reactive with water*
- *often pyrophoric, i.e., ignite upon contact with air*

Pyrophoricity Demonstration of TEAL

Photo courtesy of AkzoNobel

trimethylaluminum
methylaluminoxane
dimethylaluminum chloride
methylaluminum sesquichloride
triethylaluminum (TEAL)
diethylaluminum chloride
diethylaluminum iodide
ethylaluminum sesquichloride
ethylaluminum dichloride
isobutylaluminum dichloride
tri-n-butylaluminum
triisobutylaluminum (TIBAL)
diisobutylaluminum hydride
tri-n-hexylaluminum
tri-n-octylaluminum
di-n-octylaluminum iodide
"isoprenylaluminum"
diethylaluminum ethoxide

Principal Commercially Available Aluminum Alkyls

Citronellol-scented Polyethylene from Ziegler-Natta Catalysts

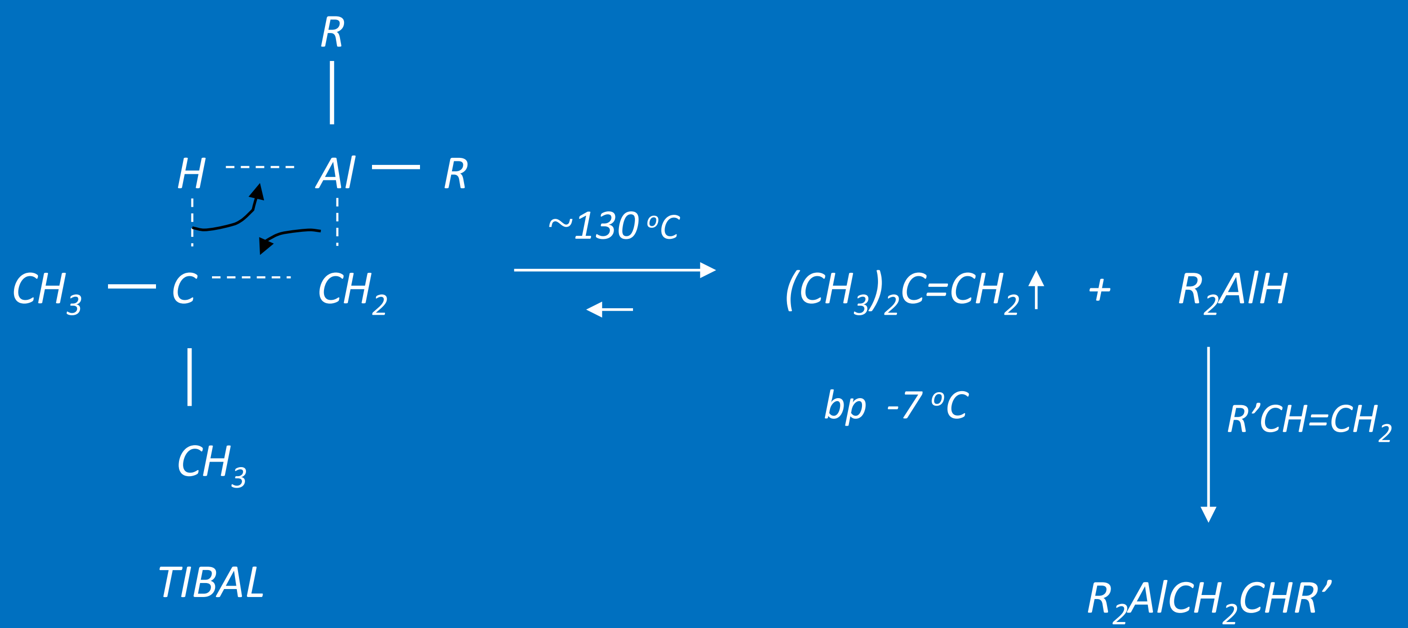
Synthesis of Tricitronellylaluminum (TCAL)

3,7-dimethyl-1,6-octadiene
aka “citronellene”

“tricitronellylaluminum” (TCAL)
aka tris (3,7-dimethyl-6-octenyl)aluminum

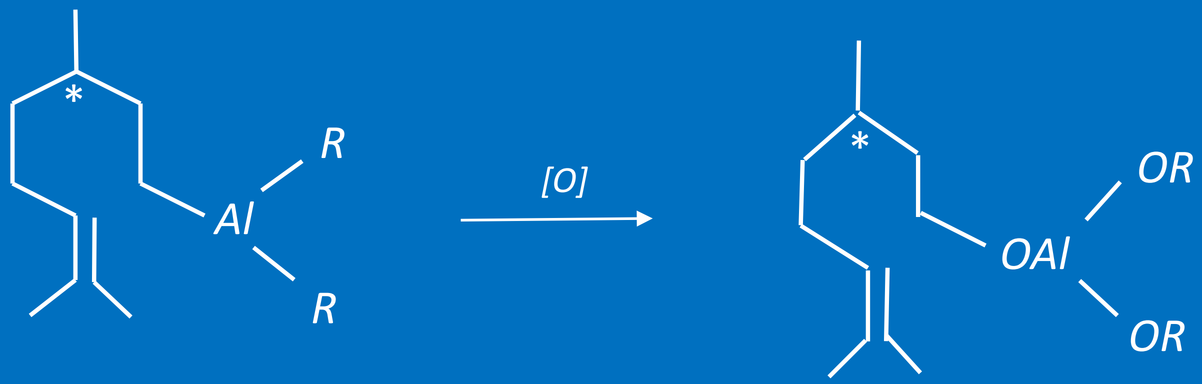
** chiral carbon atom*

Mechanism of Reaction of TIBAL with Citronellene to Form TCAL

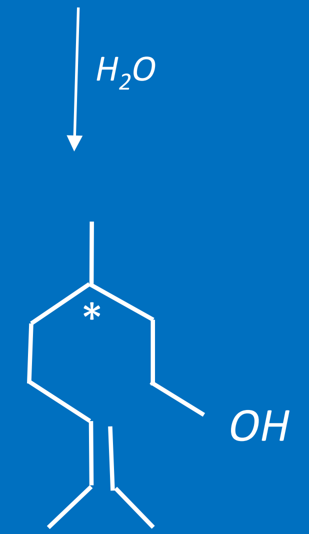


where $R'CH=CH_2$ is citronellene
(only terminal double bond in citronellene is reactive)

Conversion of TCAL into citronellol



R is a "citronellyl" group



citronellol
(aka 3,7-dimethyl-6-octen-1-ol)

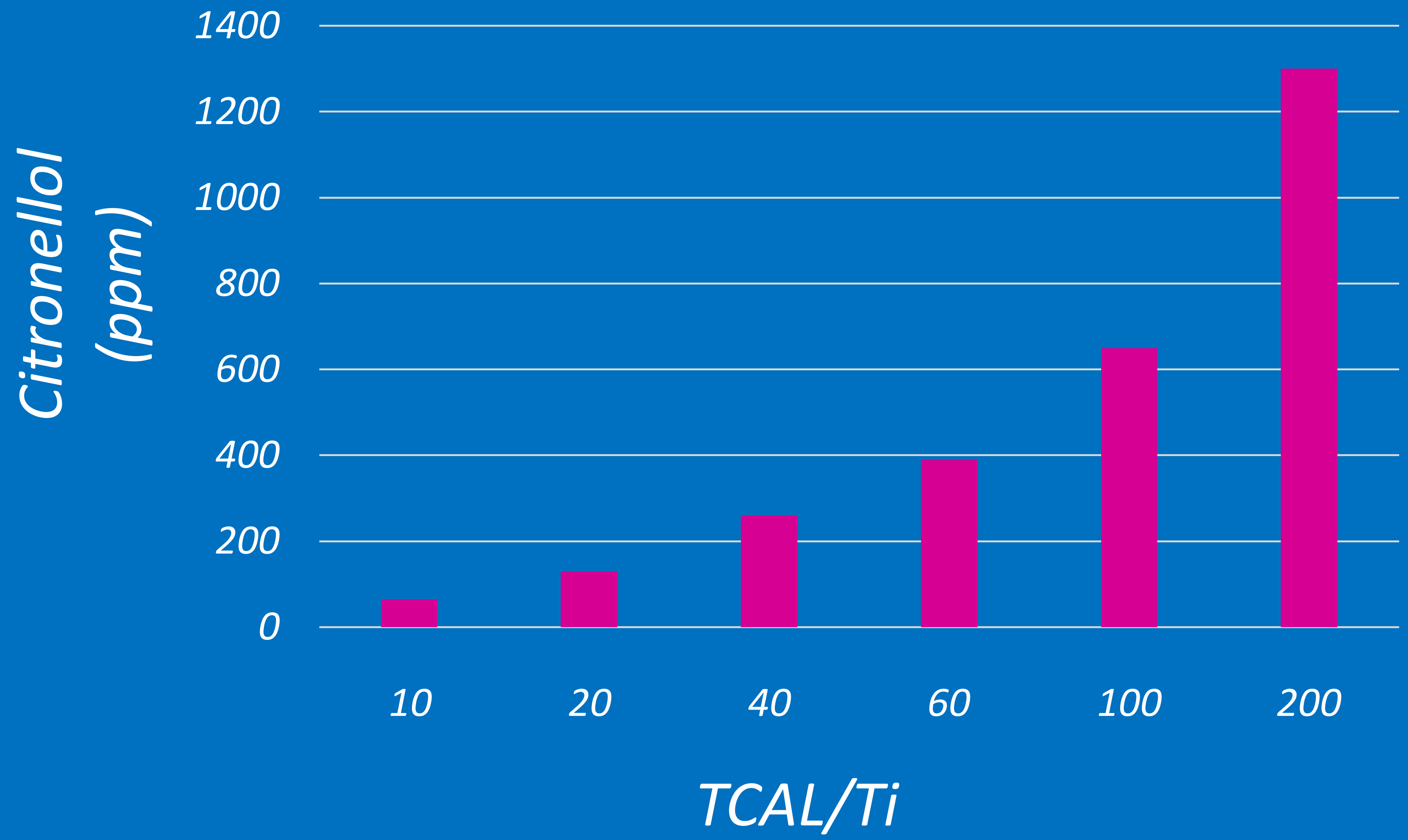
** Chiral carbon atom*

TCAL as Cocatalyst for Ethylene Polymerization

$$n\ CH_2{=}CH_2 \xrightarrow[\text{TCAL}]{\text{ZN Catalyst}} \sim(CH_2\text{-}CH_2)_n\sim$$

- ***Assumptions*:**
  - *ZN catalyst contains 1.5% Ti*
  - *TCAL cocatalyst contains 6.0% Al*
  - *Al/Ti is 40*
  - *Activity is 20,000 lb PE per lb of catalyst*
- ***Results*:**
  - *TCAL concentration in final polymer will be ~280 ppm*
  - *After oxidation/hydrolysis, citronellol concentration will be ~260 ppm*

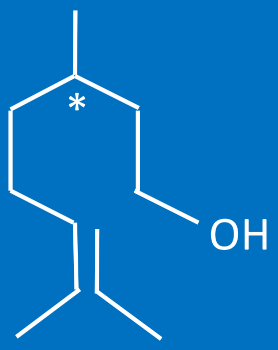
Residual Citronellol in Polyethylene



Reactivity of TCAL Compared to TEAL

- *We saw earlier a demonstration of the spectacular pyrophoricity of TEAL.*
- *TEAL is also explosively reactive with water.*
- *Pyrophoricity of aluminum alkyls is closely related to metal content.*
  - *TEAL contains 23% Al.*
  - *TCAL contains only 6% Al and is much less reactive with air and water.*

Features of Citronellol



Skeletal Structure

Molecular formula:	$C_{10}H_{20}O$
Formula weight:	*156.3*
Synonyms:	*3,7-dimethyl-6-octen-1-ol* *2,6-dimethyl-2-octen-8-ol*
Appearance:	*Clear, colorless liquid*
Boiling point:	*225 ^{o}C (at atmospheric pressure)*
Organoleptics:	*Floral, rose-like; aroma threshold detection values: 11 ppb to 2.2 ppm*
Stereochemistry	*Contains asymmetric carbon atom (*) and hence is chiral. Commercial product is mixture of stereoisomers.*
Uses:	*Perfumery, cleaning products, mosquito repellent*

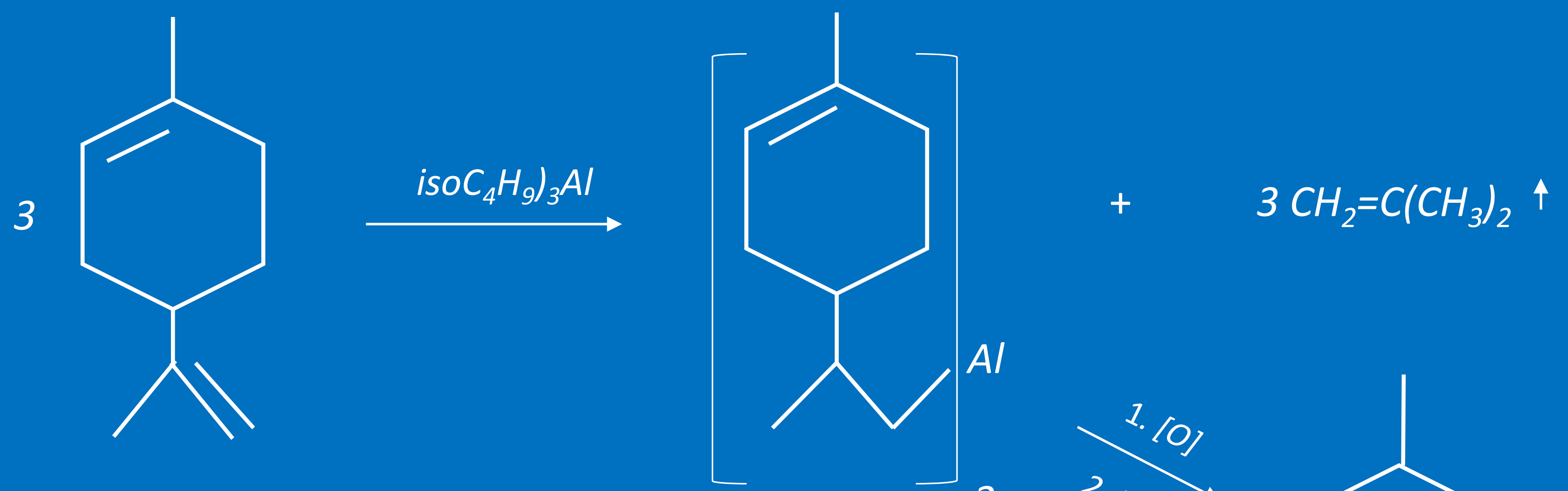
Potential Applications of Citronellol-Scented Polyolefins

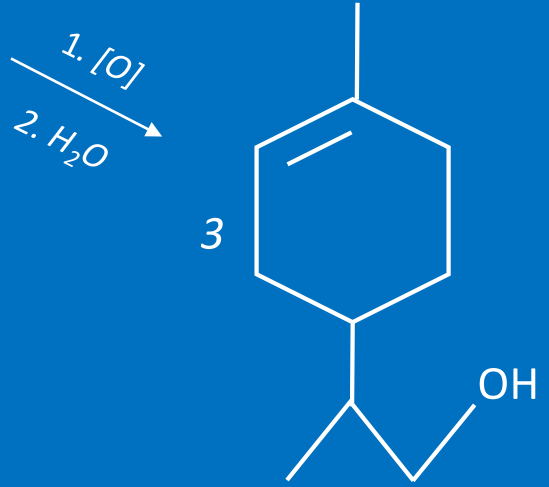
- *Plastic bags*
  - *Trash/refuse*
  - *Grocery*
  - *Merchandise*
- *Disposable diapers*
- *Personal Hygiene Products*
  - *Incontinence pads*
  - *Sanitary napkins*
- *Artificial flowers*
- *Insecticide-treated nets*

SCOPE

Other Possibilities for Scented Polyolefins

Conversion of Limonene to p-Menth-1-en-9-ol*





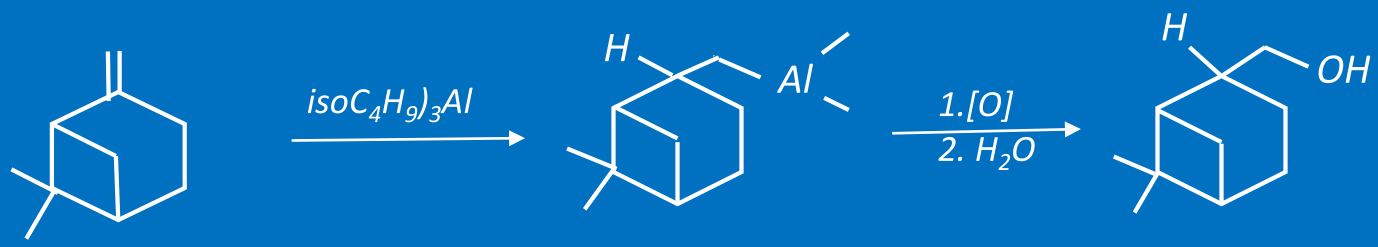
p-menth-1-en-9-ol

- *common name: limonene*
- *terpene with the scent of oranges*
- *available from rinds of citrus fruits*

- *fruity, herbal note*

*IUPAC name: 2-(4-methylcyclohex-3-en-1-yl)propan-1-ol

Conversion of β-Pinene to Myrtanol



β-pinene

- *available from pine resin*
- *woody, pine-like scent*

*Myrtanol**

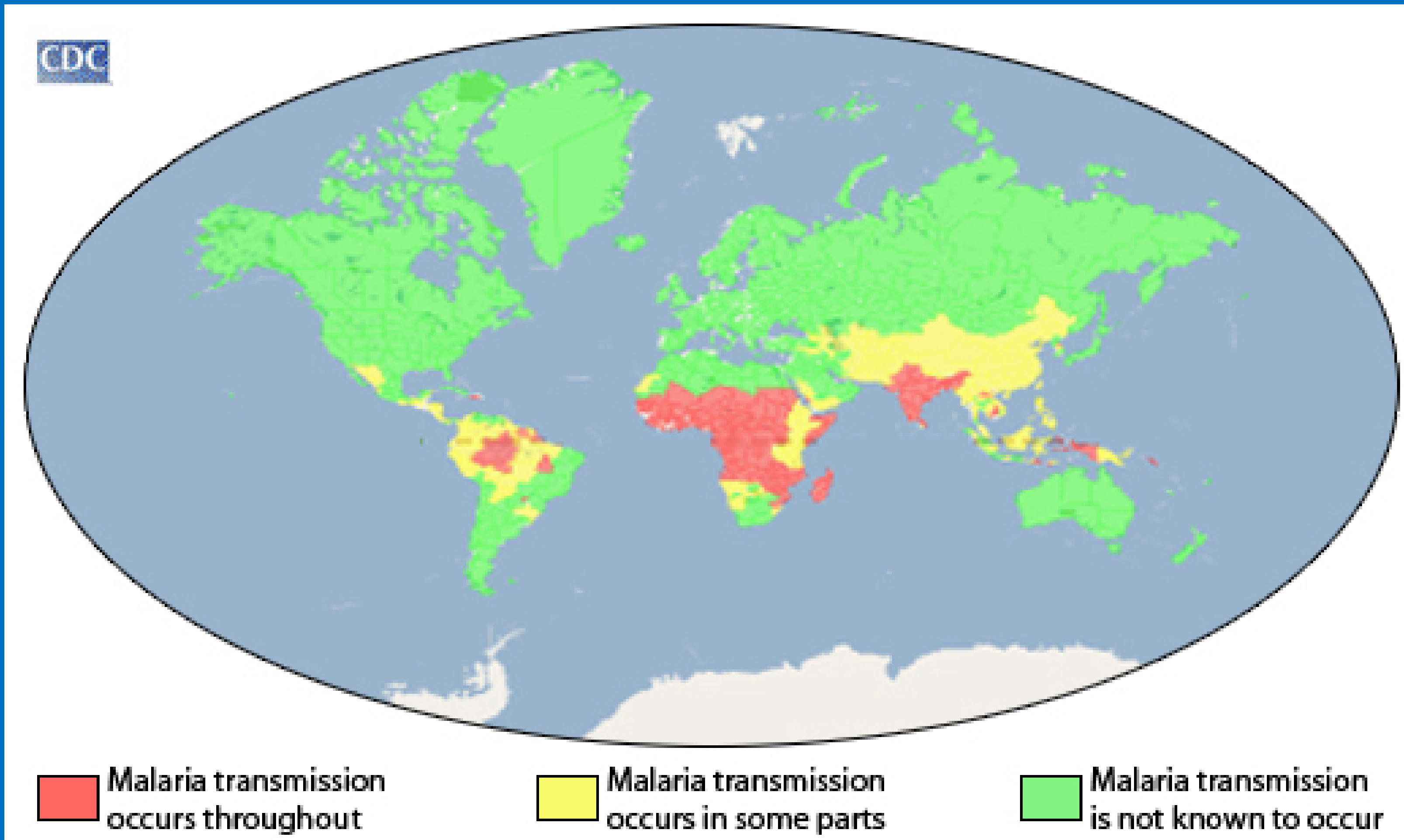
- *used in perfumery and as a flavorant*

** also known as 6,6-dimethylbicyclo[3.1.1]heptane-2-methanol (mixture of stereoisomers)*

Citronellol-Scented Polyolefins in Prevention of Mosquito-borne Diseases

Where Malaria Strikes

(Center for Disease Control)*

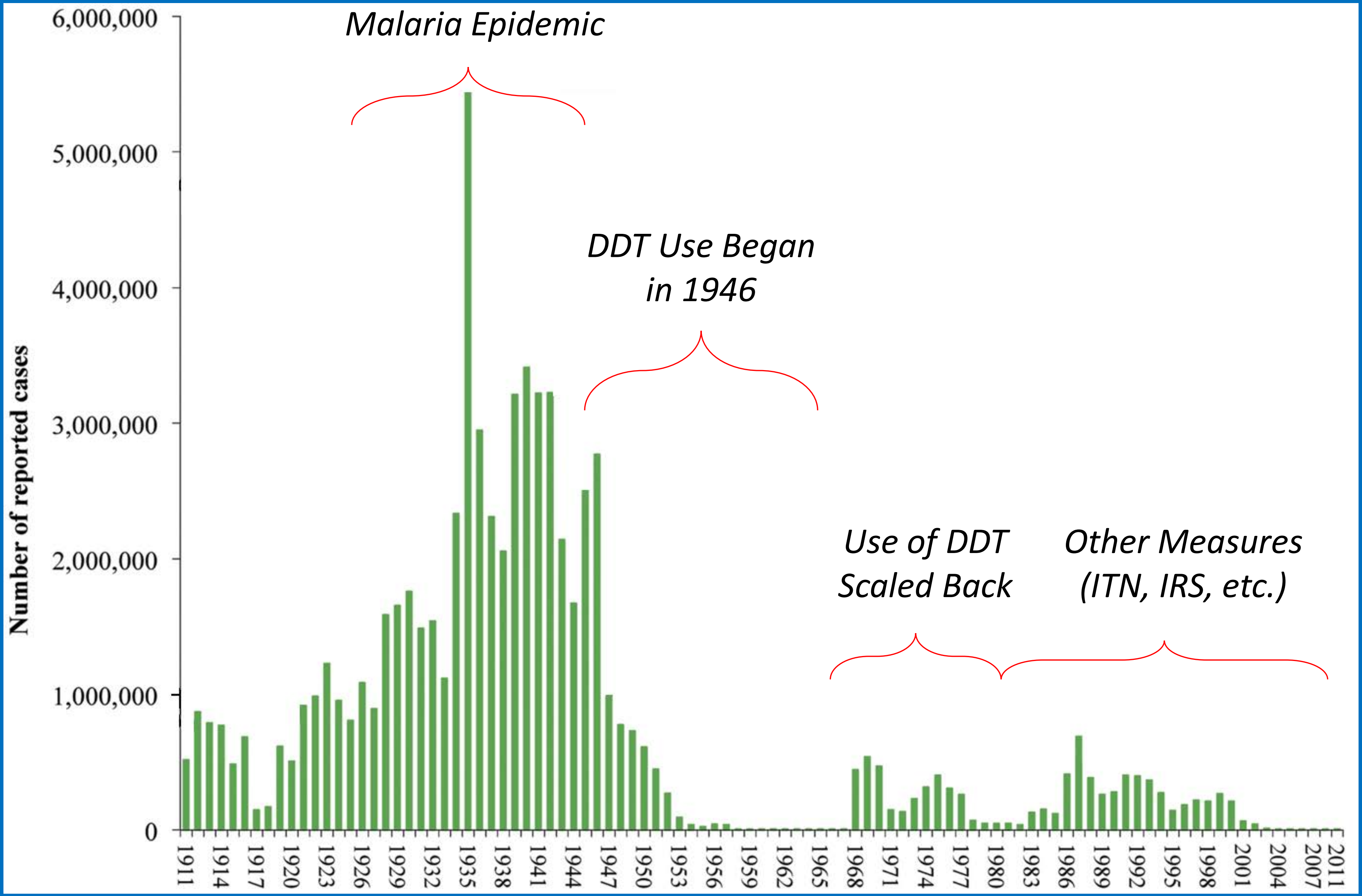


** www.cdc.gov/malaria/about/distribution.html*

Ceylon/Sri Lanka Perspective in Asia*

*www.worldatlas.com/webimage/countrys/as.htm

Case Study: Malaria in Ceylon/Sri Lanka (1911-2011)*



* *http://journals.plos.org/plosone/article?id=10.1371/journal.pone.0043162*

World Health Organization (WHO) Statement on Controlling Malaria

"Much of the success in controlling malaria is due to vector control. Vector control is highly dependent on the use of pyrethroids, which are the only class of insecticides currently recommended for ITNs…"

www.who.int/mediacentre/factsheets/fs094/en/

Vector (Mosquito) Control

- *Use of DDT decreasing because of:*
  - *bans owing to environmental concerns*
  - *increasing resistance of mosquitoes*
- *Alternative methods must be developed*
- *Two crucial methods for vector control:*
  - *Insecticide-Treated Nets (ITN)*
  - *Indoor Residual Spraying (IRS)*

Acknowledgements

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