

# Meeting New Challenges for Process Safety Excellence in Chemical Industry

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# Safety Moment



- Fire Sparked by Static Electricity
- Led to Warehouse explosion
- Warehouse person was wiping-off the spill on top of the IBC during loading
- Lesson Learnt:
  - ✓ Highly Flammable Tanks needs to be Grounded
  - ✓ When need to wipe the spill, no loading activity to be conducted

# Challenges in the Industry

- Refineries and petrochemical plants are major hazards installations
- Process safety excellence paramount importance by asset integrity and reliability
- Competition challenges led to extended turnaround intervals, use of new technologies etc.
- Also...

# Challenges in the Industry



- **Business Profitability drives feedstock options especially for Naphtha Crackers & Refineries**
  - **Regulations also dominate feedstock choices – e.g. IMO2020**
- These challenges can impact plant reliability and safety**

# Collaboration Required



- **Technology Partners can help manufacturer to improve plant reliability through technology expertise**
- **Improving Reliability improves Safety and Operational Excellence by avoiding unscheduled shutdown, less maintenance and lower energy losses**

# An Example of Positive Outcome through Collaboration

## Depropaniser Bottom Polymers Fouling

2008



Reboiler Upper Tubesheet and tube inner wall – Brownish Rubbery polymers

2008



Pressure Relief Valve's Outlet Isolation Valve plugged with polymers

Example

- Cracker plants face fouling concerns due to 1,3 Butadiene polymers
- Uncontrolled fouling can lead to plugging of reboilers, column, isolation valves and PRV
  - ✓ Safety Concern, can be catastrophic
- Eventually can result in throughput reduction and unscheduled shutdown
  - ✓ Reliability & Profitability Concern

Source: Courtesy of a Singapore Plant

# An Example of Positive Outcome through Collaboration

## Depropaniser Bottom Polymers Fouling

Example



Valve stem found worn at edges connecting with the valve disc



2008

Valve disc with worn and enlarged opening → disconnected with stem → failed to function



- Uncontrolled fouling can lead to plugging of reboilers, column, isolation valves and PRV
  - ✓ Safety Concern: loss of positive isolation can be catastrophic

# An Example of Positive Outcome through Collaboration

**Example**

**Depropaniser Bottom Fouling Condition Improved – use the right chemistries**



2011 Before

**2011 Turnaround findings – Light Brown Soft Polymers at Tower Bottom**



2016 After

**2016 Turnaround findings – Generally Clean Condition**

- Explore the right chemistries for the process
- Each process is unique by itself
- Efficient management, control and optimization of process anti-foulants

**→ Able to operate at 5-year turnaround without fouling issue**

**Reliability + Process Safety → Operational Excellence**



# Improving Operator Safety by replacing Toxic Chemicals

- **Toxic Chemicals like Nitro-Phenols (DNBP) and Dimethyl Disulfide (DMDS) important for reliable plant operations**
- **However, challenges seen in handling and waste treatment**
- **Operator Safety, Health and Environmental responsibility are of high priority**
- **Dorf Ketal has developed Innovative Chemistry to replace DNBP and DMDS**

# Replacing Nitro-Phenol

- Nitro-PDNBP – Commodity chemical used for fouling control in Styrene plants
- Though effective, it is highly toxic
  - ✓ Classified as CMR (Carcinogen, mutagenic and reproductive toxin)
  - ✓ Soluble in water and hence the risk is high
  - ✓ Generate NOx
- Banned in some countries as Herbicide in Agriculture



- Green Chemistry (Non nitro-phenol) synthesized by Dorf Ketal
- Performance and Plant Reliability improved with the use of Patented molecule in the green chemistry
  - ✓ Successful execution in Thailand, Malaysia and Indonesia
  - ✓ Plant performance and reliability significantly improved
- Extended to other monomer plant

Serious concern to Operator Safety & Health and Plant & Environmental concerns

Safer replacement of Nitro-Phenols like DNBP → Environmental friendly

# Replacing Nitro-Phenol - Hazards comparison

Hazard Category	(DNBP)	Green Replacement Chemistry	Summary
<b>Eye corrosion / irritation</b>	Eye damage 1 • H318: Causes serious eye damage	Eye Irrit. 2A • H319: Causes serious eye irritation	DNBP is more hazardous
<b>Acute Toxicity</b>	Acute Tox. 2 (oral) • H300: Fatal if swallowed Acute Tox. 3 (dermal) • H311: Toxic in contact with skin	Not Classified	DNBP is acutely toxic via oral and dermal
<b>Reproductive Toxicity</b>	Repr. 1B • H360Df: May damage the unborn child. Suspected of damaging fertility	Not Classified	DNBP is suspected of causing reproductive toxicity
<b>Acute Aquatic Toxicity</b>	Aquatic Acute 1 • H400: Very toxic to aquatic life	Not Classified	DNBP is acutely toxic to environment
<b>Chronic Aquatic Toxicity</b>	Aquatic Chronic 1 • H410: Very toxic to aquatic life with long lasting effects	Aquatic Chronic 3 • H412 Harmful to aquatic life with long lasting effects	DNBP is more chronically toxic to aquatic environment

# Replacing Dimethyl Disulfide (DMDS)

- **DMDS – Sulfiding Agent used in Refineries and Petrochemical Plants**
  - ✓ For Catalyst Pre-sulfiding
  - ✓ Furnaces in Steam Cracker
- **Also used in the manufacture of pesticides**
- **Difficulty in handling**
  - ✓ Low Flash Point (16° C)
  - ✓ Volatile
  - ✓ Strong Odor
  - ✓ High Toxicity



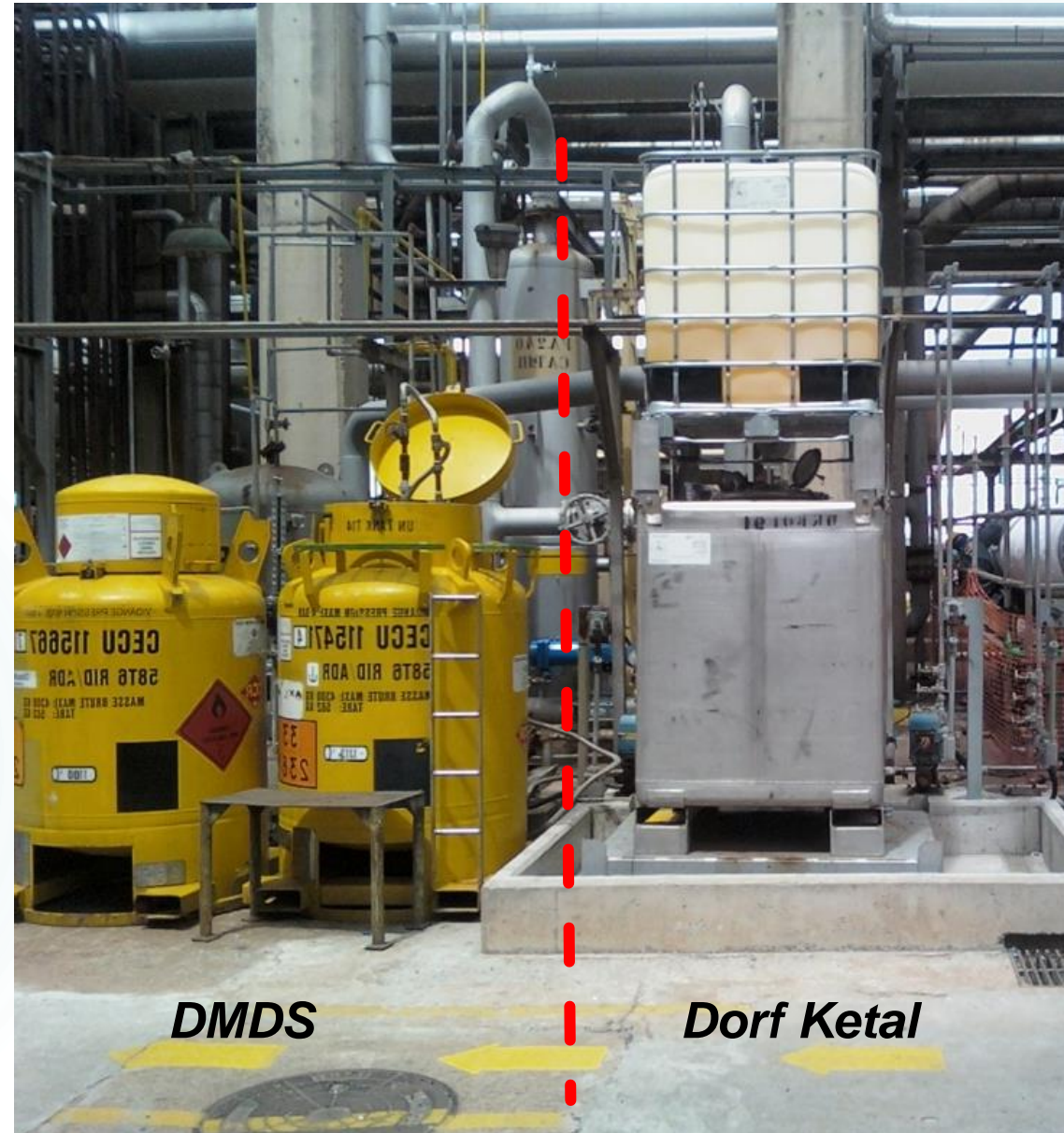
- **Safer Replacement**
- **Attributes**
  - ✓ Higher Flash Point ( > 65° C)
  - ✓ Low Odor
  - ✓ Easy Storage conditions
- **Can be used for improved performance of equipment**

Operator Safety and Health Concerns

Supports plant operations in Safety and Reliability

## DMDS Handling

- Use of Nitrogen pressure when transferring chemical
- Disposal of DMDS / residue in tanks is a challenge



## Dorf Ketal

- Easy Storage
- No Nitrogen / flaring system required
- Easy pump maintenance

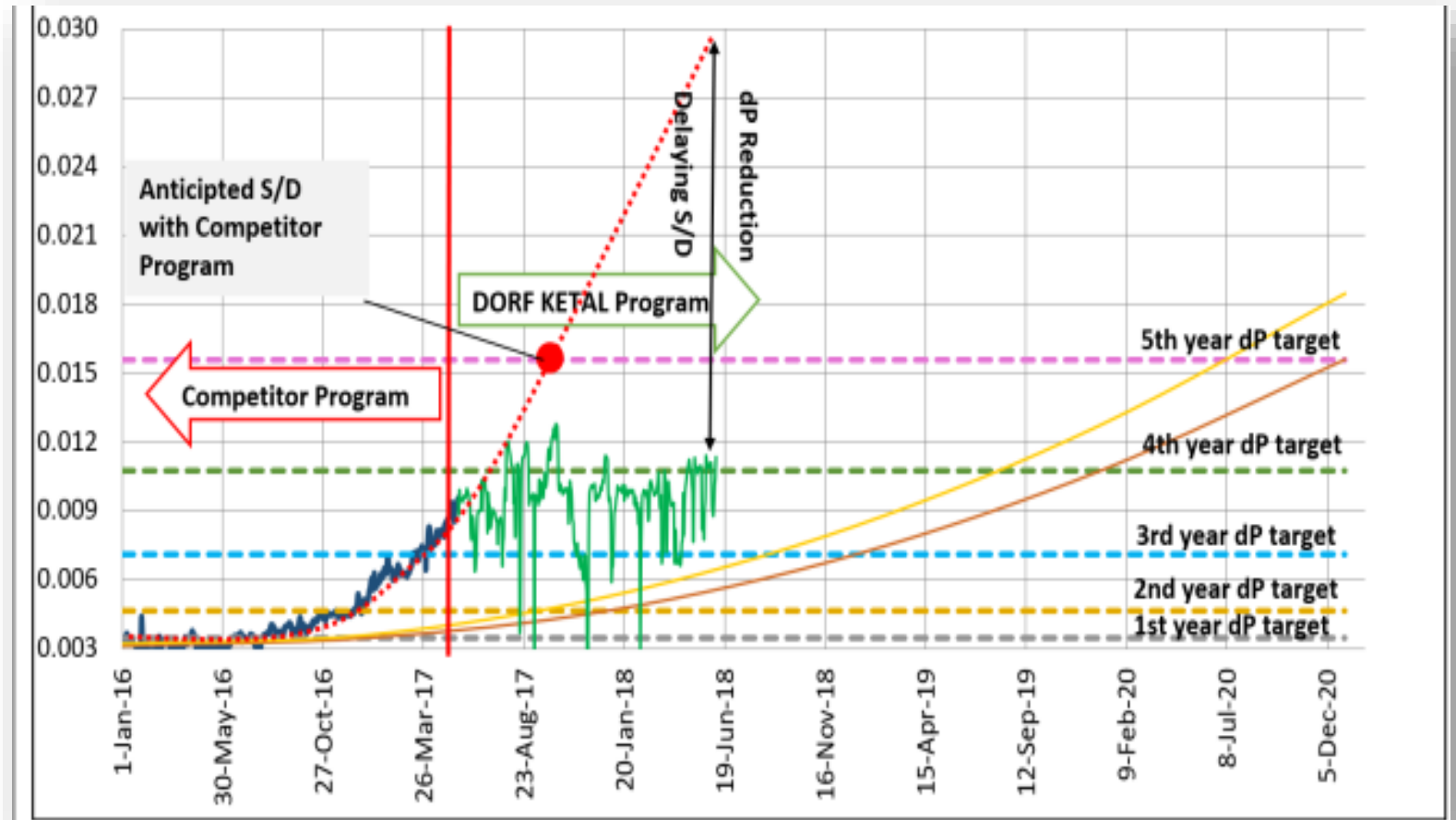
# Value-add Offering – Avoid Unscheduled Shutdown

- **Fouling and Corrosion issues are challenges faced by many manufacturers which impact plant reliability and process safety**
  - ✓ Equipment fouling can lead to frequent maintenance activities
  - ✓ Corrosion can lead to leaks and loss of containment which can have catastrophic impact
  
- **Unscheduled shutdowns / turnarounds and plant upsets impact plant process safety**
  - ✓ Higher Risk activities to be avoided during turnaround
  - ✓ Some polymers are pyrophoric – hence a concern to plant and equipment safety during maintenance / turnaround

# Value-add Offering – Improving Plant Reliability Examples

- Cracker in South-East Asia
- Fouling could have led to unscheduled shutdown
- With Dorf Ketal program, shutdown could be delayed and plant reliability improved especially in downstream units

Column Differential Pressure (dp) – Caustic Tower



Avoided unscheduled shutdown → eliminated Higher Risk (process safety) activities

# D O R F K E T A L

**DRILLING OIL**

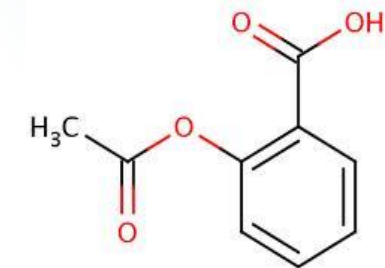
**OLEFINS**

**REFINING**

**FUELS**



***Strong in Research, Product  
technology & Technical  
competence***



- **Market Leaders for Specialty Chemicals**
- **Focused on Process Side Treatment for Refinery, Petrochemical and Fuel Additives**



## Dorf Ketal can offer

### ➤ Opportunity Value

- ✓ Anti-foulants when processing challenging feedstocks
  - E.g. Anti-foulants for Compressors, Anti-foulants for Gasoline / Fuel Oil-riched columns, Corrosion control for high acidity crudes, de-emulsifiers for opportunity crudes
- ✓ Decontamination of Columns for safer and quicker man-entry
- ✓ Replacement of toxic DMDS and DNBP chemicals

### ➤ Preventive Value

- ✓ E.g. Corrosion Control Programs, Fouling control for Butadiene and Styrene plants
- ✓ Achieve finished fuel specs to minimize reprocessing / blending costs

### ➤ Restorative Value

- ✓ Restore energy losses or delay shutdown by improving column run-length through anti-foulants

# Methodology for Treatment Program Collaboration with Recommendation

- **Understand Process Conditions**
- **Gather Information of past incidents / deviations and operational changes**
- **Collaborate with Manufacturer**
  - ✓ Chemistry expertise
  - ✓ Sharing experience
  - ✓ Customize with Plant challenges (if required). For example: formulation customized for plan changes (antioxidants, corrosion control etc.)
- **Develop Test Plan**
  - Identify Leading indicators (symptoms) and recommend tests and solution trails

- **Refinery – Processing High Acidity Crude with better corrosion control programs**
- **Resolving emulsions to ensure smoother wastewater treatment**
- **Improving plant run-length of Butadiene, Styrene and Olefin plants by better fouling control**

# Proactive Process Conditions Monitoring

- **Dorf Ketal invests in analytical and simulation monitoring tools to predict fouling and corrosion potential**
- **These tools guides the operators and Dorf Ketal service team towards smoother plant operation and proactive monitoring**
- **Taking Proactive steps for better plant reliability and Operational Excellence**



**Manufacturer improves profitability by engineering solutions like debottlenecking, revamping and feedstock choices**

**Dorf Ketal can collaborate for fouling, corrosion and emulsion control solutions to improve plant reliability and ensure “Avoid Unscheduled Shutdown” – eliminate high risk (process safety) activities**

**Manufacturer can:**

- (a) achieve Operational and Safety Excellence**
- (b) improve Operator Safety and Health by replacing toxic chemicals**
- (c) achieve Sustainable Business Plan**

# Conclusion

- **Managing risks by ensuring asset integrity and reliability for hydrocarbon processing facilities is challenging**
- **Asset integrity and reliability and process safety are keys to operational excellence for profitability**
- **Use the right chemistries via chemical treatment for mitigation measures for issues arising from upstream technological changes**
- **Collaborate with a partner of chemistry expertise, rich in experience and willing to customize with challenges**

**Thank You**