

ENGINEERING DESIGN SEMINAR

SEPTEMBER 6, 1994 – NOVEMBER 11, 1994

FUEL ADDITIVES

By M.W. Schrepfen

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FUEL ADDITIVES

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GASOLINE

Origin

Blend Component	Process Unit
Straight Run Naphthas	Crude Unit
Cat Gasoline	Fluid Cat Cracker
Alkylate	HF or H ₂ SO ₄
Poly Gasoline	C ₃ /C ₄ Polymerization
Coker	Coke Production
Reformate	Platformer, Isomerization
MTBE, TAME, ETBE	UOP & Others
Alcohols	Methanol, Ethanol

Important Properties

Property	Influenced By
Volatility	Distillation Range
Antiknock Quality	Hydrocarbon Type/Additives
Energy Content	Hydrocarbon Type
Density	Hydrocarbon Type
Viscosity	Hydrocarbon Type

Octane No.
2. 150 octane 150

GASOLINE QUALITY DEFICIENCIES

Available Solutions

	Chemical	Process
Low Antiknock	Yes	Yes
Rust Protection	Yes	No
Combustion Deposits	Yes	No
High Mercaptan Level	Yes	Yes
Storage Instability	Yes	Yes
Wrong Color	Yes	No

Sweetening
Sediment Blending

GASOLINE

Remedies for Deficiencies

Low Octane

- Lead Alkyls – Tetraethyl lead and tetramethyl lead
- MMT – Methylcyclopentadienyl manganese tricarbonyl

Rust Protection

Corrosion Inhibitors:

- High molecular weight organic acids
- Amine salt of phosphate acid
- Dimerized linoleic acid

Contribution to Deposits

Deposit Control Additives:

- Organo phosphate compounds
- Polyisobutenyl amines
- Polyisobutenyl succinimides
- Polyether amines
- Polyamino polyols (UOP® GA-6™ additive)

Wrong Color

Dyes:

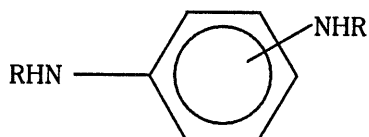
- Organic ashless compounds

Sour Fuel (High Mercaptans)

Inhibitor Sweetening Agents:

- N, substituted phenylenediamines

*Gasoline
Inhibitor Sweetening*



N, substituted phenylenediamines

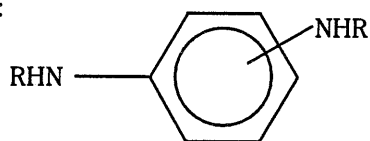
UOP® No. 5™
UOP No. 17-P™

UOP No. 5-s™
UOP No. 18®

UOP No. 12-P™

Need:	Inhibitor	5-20 wt ppm
	Olefin	> 2%
	Caustic	Trace Amount
	Oxygen	2 x Theoretical
	Time	2-6 Days

Overall Reaction:



EDS-R00-1620

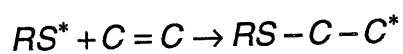
GASOLINE

Mechanism of Inhibitor Sweetening

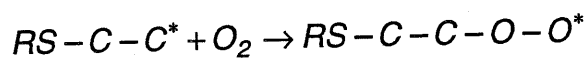
Step 1:



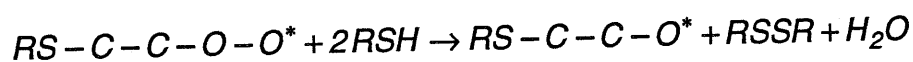
Step 2:



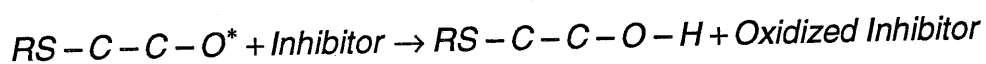
Step 3:



Step 4:

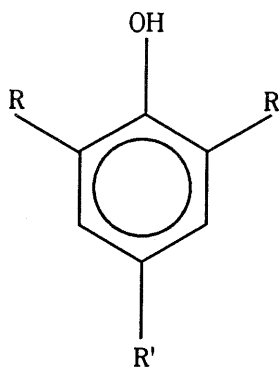


Step 5:



*Gasoline
Remedies for Deficiencies*

- Storage Instability
Hindered phenols



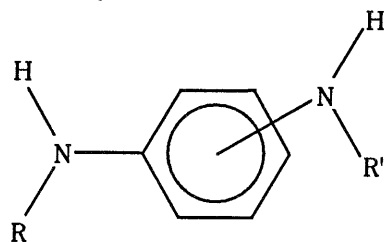
R = Butyl alkyl group
(s-Butyl, t-Butyl. etc..)
R' = R, H, CH₃

UOP® No. 344™ (R = t-Butyl, R' = H)
UOP No. 7™ (R = t-Butyl, R' = Methyl)

EDS-R00-1621

*Gasoline
Remedies for Deficiencies*

- Storage Instability
Phenylenediamines

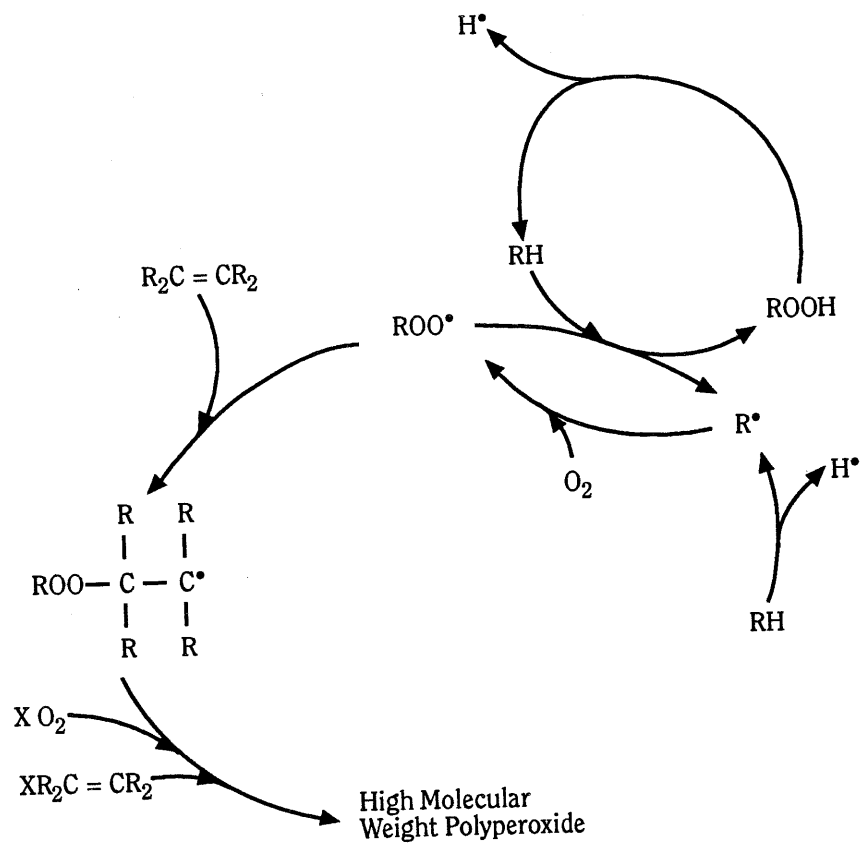


R = s-Alkyl
R' = R, Phenyl

UOP® No. 5™ (R = R' = s-Butyl)
UOP® No. 12-P™ (R = s-Butyl, R' = Phenyl)
UOP® No. 16/18™ (R = R' = s-butyl, ortho)
UOP® No. 17-P™ (Mixed)

EDS-R00-1622

*Gasoline
Storage Stability: Free Radical Reaction*



Net Results: High molecular weight polymers containing carbon, hydrogen, oxygen, and small amounts of sulfur

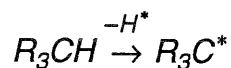
EDS-R00-1623

GASOLINE

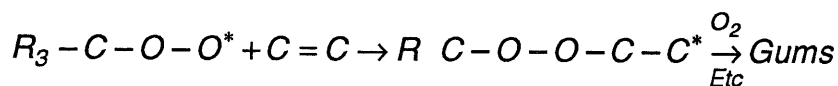
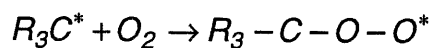
Oxidation Inhibition – Mechanism

to prevent Gums.

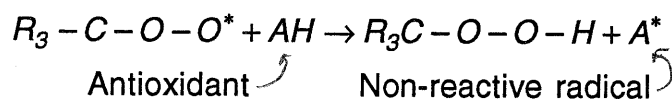
Initiation:



Propagation:



Termination:



*much faster
- 1000x*

Characteristics of Blend Components

Straight Run Gasoline

Low olefins (< 5 pct)

Good stability (gums: < 5 mg/100 ml)

*potential gum
rise 4 hr*

FCC Gasoline

High olefins (30–60 pct)

Some diolefins (0.1–3 pct)

Poor stability (gums: 20–200 mg/100 ml)

Thermally Cracked Gasoline

Very high olefins (50–80 pct)

High diolefins (2–10 pct)

Very poor stability (gums: 200–1000 mg/100ml)

Poly Gasoline

Very high olefins (80–100 pct)

Very low diolefins (< 0.5 pct)

Anomalous stability (gums: < 5 mg/100 ml)

Platformate Gasoline (Reformate)

Low olefins (< 5 pct)

Good stability (gums: < 5 mg/100 ml)

Existent Gum ASTM D-381
0.5

Storage Stability Remedies

Blend Only Straight Run Stocks

Not practical

Hydrotreat Cracked Stocks to Remove Olefins

Lose octane value

Expensive

Chemically Treat

Antioxidants – interrupt chain reaction

Phenylenediamines

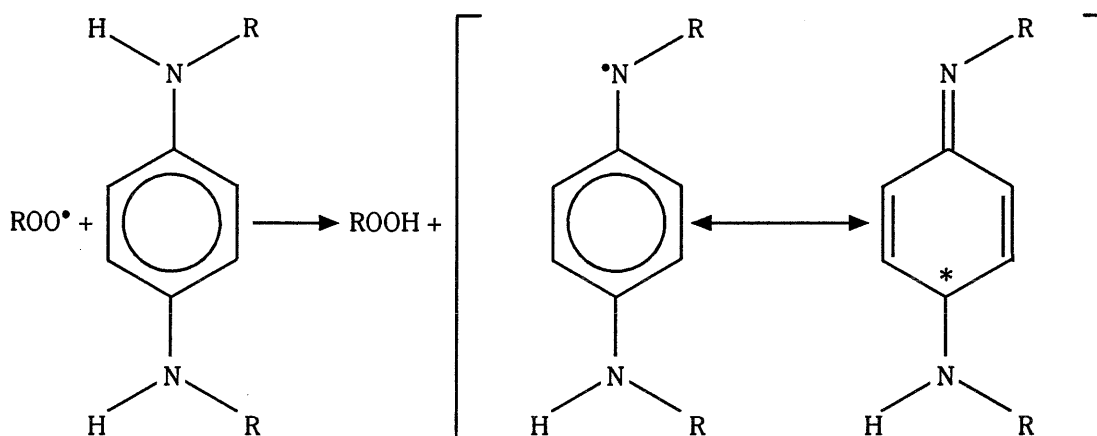
Hindered phenols

Metal deactivators – chelate metallic ions

Gasoline Antioxidants: Stabilize Peroxy Free Radical

Phenylenediamines:

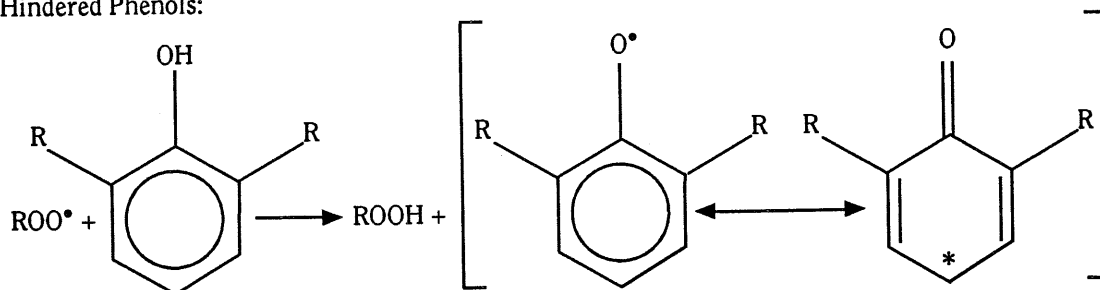
very strong



EDS-R00-1624

Gasoline
Antioxidants: Stabilize Peroxy Free Radical

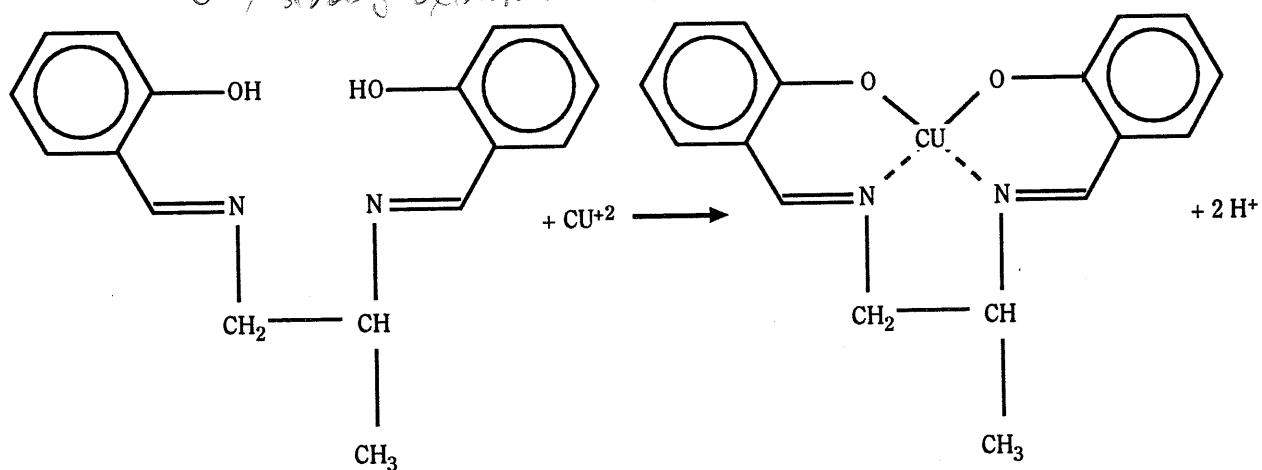
Hindered Phenols:



EDS-R00-1625

Gasoline
Metal Deactivators: Chelate Metal Ions

Very strong oxidizing material



EDS-R00-1626

Chemical Dosing Rates

Phenylenediamines

4–40 wt ppm

1–10 PTB

pound per thousand barrel

Hindered Phenols

12–120 wt ppm

3–30 PTB

Metal Deactivators

0.8–8 wt ppm (active ingredient)

0.2–2 PTB (active ingredient)

Added Benefits of Chemical Treating

Phenylenediamines catalyze sweetening

Cost effective

Protection to point of use

Develop an Effective Treating Scheme

Use fresh samples – excluding air and light

Determine stability of components

803 = method
oxidant gums ASTM-D381 modified 4 hour potential gum test

Stability criteria of pool: $< 5 \text{ mg/100 ml}$ = Chemical Group Guideline

Optimize antioxidant dosage

Dose fresh sample with several AOX's at various levels

Determine inhibited gum formation rate

Confirm findings with 110°F long-term dark storage

Treat unstable components at optimum dosage in run down line

DIESEL FUEL

High H₂ Sulfur, type of reaction

Origin

Severity of Sulfur

Component	Process Unit
Straight Run LGO	Crude Unit
Straight Run HGO	– Hydrotreated
Straight Run Kerosine	– Merox Sweetened
Light Cycle Oil	Fluid Cat Cracker
Thermally Cracked	Coker/Visbreaker
Hydroprocessed	Hydrocracker/Hydrotreater

used
separate
process

Important Properties

Property	Major Influence
Hydrocarbon Composition	Crude/Component
Ignition Quality	Hydrocarbon Type
Energy Content	Hydrocarbon Type
Volatility	Distillation Range
Density	Hydrocarbon Type
Pour Point	Hydrocarbon Type
Flash Point	Volatility
Carbon Residue	Hydrocarbon Type
Ash Content	Crude/Processing
Corrosivity	Sulfur Content/Form
Stability	Processing/Crude
Sulfur Content	Crude/Processing

DIESEL FUEL QUALITY DEFICIENCIES

Possible Solutions

	Chemical	Process
<i>Cetane properties</i> Poor Ignition Quality	Yes	Yes <i>aromatics add cycle</i>
Rust Protection	Yes	No
Biological Attack	Yes	No
Poor Cold Flow Properties	Yes	Yes
Instability	Yes	Yes <i>hydrocracking</i>
Too Smoky	Yes	Yes <i>hydrocracking</i>

DIESEL FUEL

Remedies for Deficiencies

Poor Ignition

Cetane improvers:

Alkyl nitrates UOP® Cetro 100™ additive

Rust Protection

Rust inhibitors:

High mol wt carboxylic acids

High mol wt amines

Unicor® J inhibitor

Unicor M inhibitor

Biological Attack

Biocides:

- Organoboron compounds

Poor Cold Flow Properties

• Cold flow improvers:

- Medium mol wt co-polymers
 - Acrylates, styrenics, ethylene–vinylacetates
 - Polyflow[®] 6100, 6200, 6300, 6400 additives

Remedies for Deficiencies

Too Smoky

• Smoke depressants:

- Organobarium compounds

Poor Electrostatic Conductivity

Antistats:

- Quaternary ammonium compounds

Instability

Stabilizers:

Secondary amines

Polyamino polyols

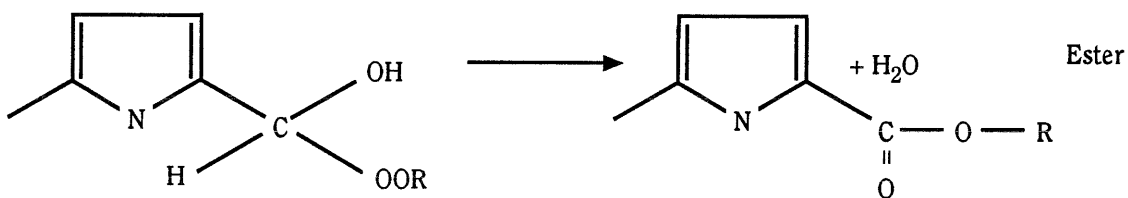
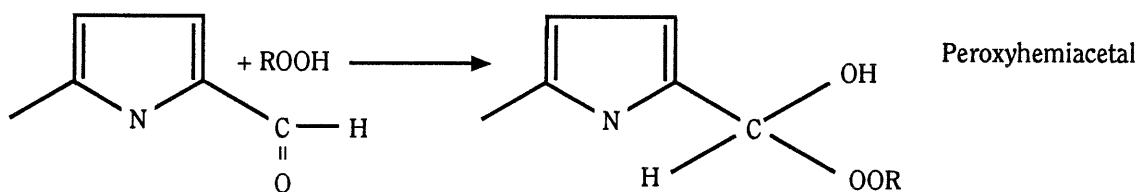
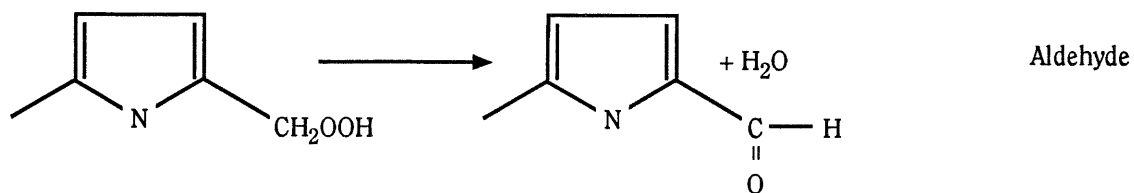
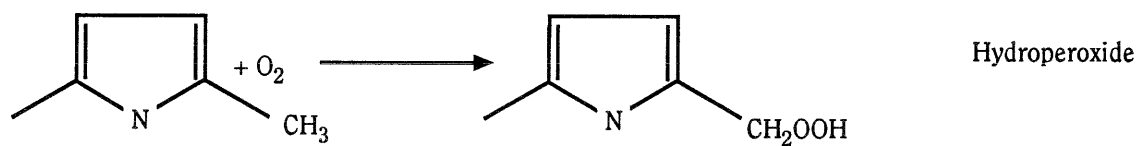
Color

Stabilizers

Dyes:

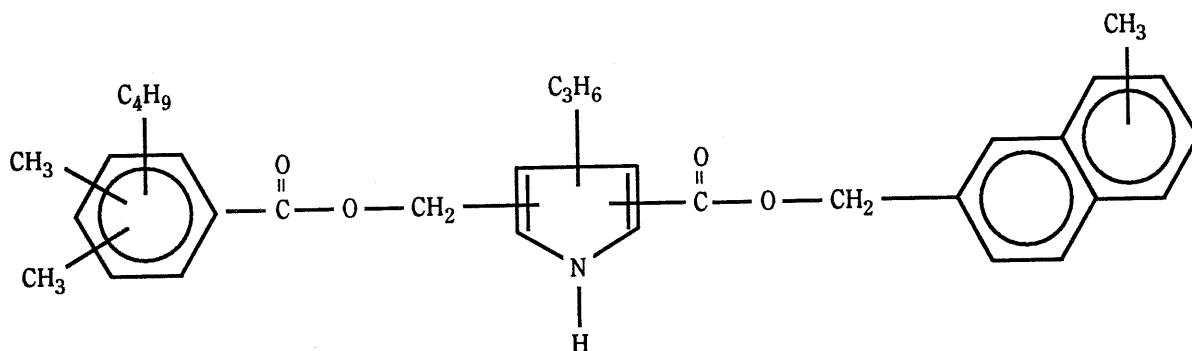
High sulfur off-road diesel – blue

*Diesel Fuel
Causes of Instability*



EDS-R00-1627

***Diesel Fuel
Typical Sediment Molecule***



filterable material
25 μm
0.5 μm

Sediment Composition

Carbon	60 - 78%
Hydrogen	6.0 - 7.5%
Nitrogen	1.5 - 2.8%
Sulfur	0.9 - 3.6%
Oxygen	7.4 - 17.5%

M.W. About 500

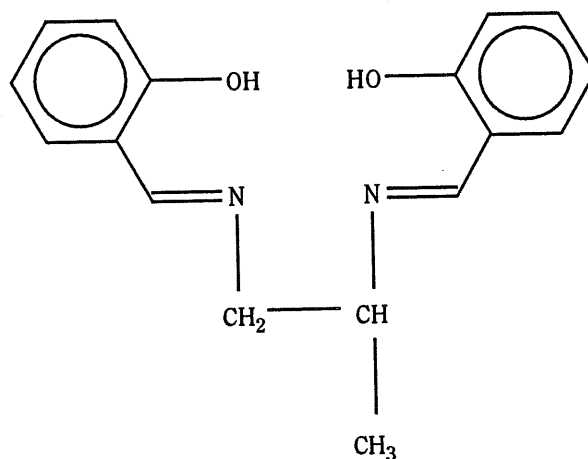
Am
10
100
200

Formation catalyzed by thiophenols or Metallic ions.

EDS-R00-1628

***Diesel Fuel
Stabilize Metallic Ions***

N, N' - Disalicylidene - 1, 2 - Diaminopropane



EDS-R00-1629

DIESEL FUEL

Instability

Oxidation of Trace Contaminants

Straight run stocks:

Low contaminants

Good stability

Sediment*: < 2 mg/100 ml

Gums*: < 20 mg/100 ml

Cracked stocks:

High contaminants

Poor stability

Sediment*: > 2 mg/100 ml

Gums*: > 20 mg/100 ml

1.8 mg UOP

one day

*After 1 year storage under moderate climatic conditions.

Problems Associated With Instability

Plugging of fuel filters

Injector and pump wear

Varnish/gum deposits on injectors and pumps

Coked injector nozzles

Color degradation

These result in:

Hard cold-start

Noisy warmed-up operation

High fuel consumption

CONSUMER DISSATISFACTION!

Complicating Factors

Increased demand for distillates

Decreased demand for residuals

Steady demand for gasoline

ALL RESULT IN HEAVIER USE OF CRACKED STOCKS

Crude quality decline

Heavier

Higher sulfur

Higher metals

Increased use of synthetic crudes

ALL RESULT IN HIGHER LEVELS OF CONTAMINANTS IN DIESEL FRACTIONS

Instability Remedies

1. Blend Only Straight Run Stocks

Not economically practical

2. Hydrotreat Remove to Heteroatoms

Reduces sulfur (EPA regulation limits sulfur content)

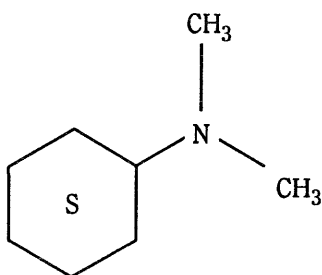
Improves cetane (some due to aromatics saturation—EPA regulation)

Decreases gravity (some) *expensive*

Expensive (\$1.50–\$2.00/bbl)

Diesel Fuel Instability Remedies

2. Chemical Treatment Stabilizers – interrupt chain reaction



POLYFLO 195™

Dispersants – stop particle agglomeration
Polymeric acrylates
Polyamino polyols POLYFLO 130™

EDS-R00-1630

Instability Remedies

Detergents

Polyamino polyols (DA-4387™)

Metal Deactivators

N, N'-Disalicylidene 1,2-Diaminopropane

N,N'-Disalicylidene 1,2-cyclohexanediamine

Developing an Effective Treatment Scheme

Fresh Samples

Exclude light and air

Determine Stability of FINISHED BLEND

UOP® 413™ Accelerated Aging Test

16 hours @ 212 °F, 1 atm O₂

Stability criterion

< 1.6 mg/100 ml

Determine Most Effective Stabilizer and Optimize Dosage

Confirm Findings With 100 °F Long-Term Dark Storage

Treat Least Stable Compound With Sufficient Additive to Stabilize Finished Blend

Inject into run-down line ASAP

Instability Remedies

Typical Chemical Treating Dosage Rates

Stabilizers:

10–60 wt ppm, 3–18 PTB

Detergents:

50–200 wt ppm, 15–60 PTB

Dispersants:

10–60 wt ppm, 3–18 PTB

Metal deactivator:

0.8–8 wt ppm A.I., 0.2–2 PTB A.I.

50–600 ppm.

Cetane promoter : low volume % Cetane.

low : very difficult to start engines, smoke
high : very fast light on

JET FUEL

Origin

Component	Process Unit
Hydrotreated Distillates	Crude Unit Distillation Hydrotreating
Straight Run Kerosine	Crude Unit Distillation Merox Treating
Hydrocracked Gas Oils	Hydrocracking

Important Properties

Property	Influenced By
Hydrocarbon Composition	Crude Source, Processing
Energy Content	Hydrocarbon Composition
Volatility	Distillation Range
Pour/Freeze Point	Hydrocarbon Composition, Distillation Range
Flash Point	Volatility
Corrosivity	Sulfur Content/Form
Stability	Processing <i>blending</i>
Luminosity	Hydrocarbon Composition <i>aromatic</i>
Ash Content	Crude Source, Processing
Lubricity	Hydrocarbon Type, Purity, Sulfur

JET FUEL QUALITY DEFICIENCIES

Possible Solutions

	Chemical	Process
Electrical Conductivity	Yes	No
Rust Protection	Yes	No
Lubricity	Yes	No
Peroxide Formation	Yes	No
Water Crystallization	Yes	Yes

JET FUEL

Chemical Treatment Remedies

Conductivity

Antistat – ammonium salts

Rust Protection

Corrosion inhibitors – organic acids:

UOP Unicor J™

Lubricity

Lubricity improvers – organic acids:

UOP Unicor J corrosion inhibitor

Water Crystallization

Anti icers:

Glycols and ethoxylated glycols

Union Carbide

Peroxidation

Antioxidants – hindered phenols:

UOP No. 344 antioxidant

RESIDUAL FUEL

B/C. No. 6

Characteristics and Effects on Combustion

Characteristics

High sulfur content

High metal content:

Vanadium

Nickel

Sodium

High particulates : *corrosive compounds*

Results of Combustion

Corrosive combustion products (SO_3)

Heavy slag deposits (metal oxides)

Coked/fouled burner tips

Effect on Equipment

Boiler tube failure (perforation)

Decreased heat transfer

Decreased burner life

Chemical Treating and Effects

Chemical Treating

Slag modifier:

MgO (disperses solids)

Organomagnesium compounds fuel soluble

Detergent/dispersant:

Polymeric amine

Effects of Treating

Neutralize acids in fuel

Modify slag chemistry:

Looser, fluffier deposit

Cleaning/decoking of burner tips

UOP FUEL ADDITIVES

Antioxidants

UOP® No. 5™

UOP No. 5-S

UOP No. 6

UOP No. 7 *BHT*

UOP No. 12-P

UOP No. 17-P

UOP No. 18

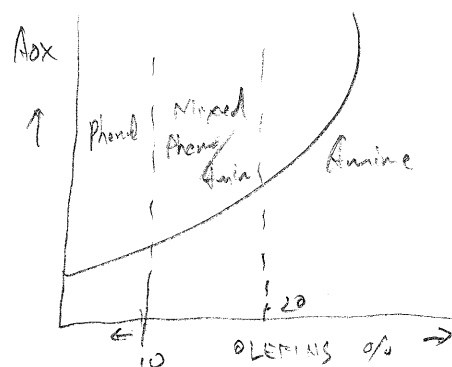
UOP No. 344

UOP No. 3425

UOP No. 3455

UOP No. 3457

Consd effective



Fuel Oil Stabilizers

Polyflo® 195

Polyflo 196

Polyflo 197

Polyflo 128

Metal Deactivators

Regular Grade

AWTM-50

Multifunctional Fuel Additives

UOP GA-6

UOP DA-4387 *for diesel fuel*

Cold Flow Improvers

Polyflo[®] 6100

Polyflo 6200

Polyflo 6300

Polyflo 6400

Corrosion Inhibitors

Unicor[®] JTM

UnicorTM MTM *fuel pipe line formation system*

Cetane Improver

CeproTM 100

SUMMARY

Most fuels as produced are unsuitable for end use.

Remaining deficiencies are chemically remedied.

Low octane	Gasoline
Low cetane	Diesel
Sour	Gasoline
Rust protection	All
Unstable	All
Wrong color	All
Biological attack	Diesel
High pour point	Diesel
Smoky	Diesel/jet
Low electrical conductivity	Diesel/jet
Low lubricity	Diesel/jet

FUEL ADDITIVES

By M.W. Schreffer

Chemical Treatment

Octane = Energy Content.

FCC Gasoline

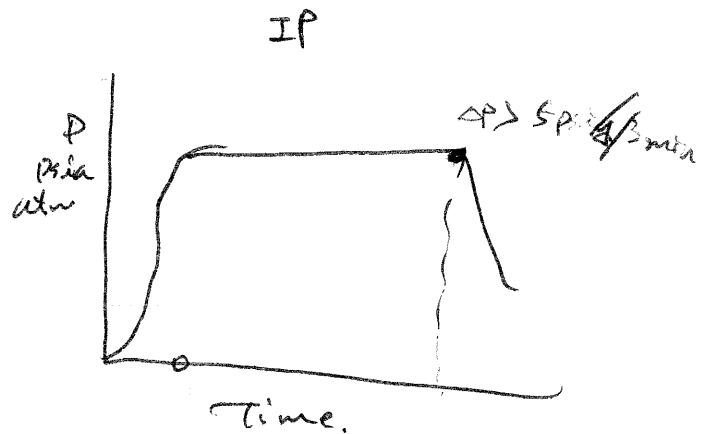
D-893 4hr Pot. Gum

D-525 Inductive Period

FCC GASO

IP 1200 min

POT Gum 20 ~ 150 mg/100 ml.



Temp 100°C

ASTM IP: ASTM 240 min
UOP 300 min

4 x 60 = 240 min.

4hr. Pot. 4 hrs @ 100°C & 100 psia O₂.

Measure gum ASTM D381

required

ASTM spec. GASO.

- RESISTANT GUM < 2 mg/100 ml. = at the point of use
- IND. PER > 240 min. = not the point of sale

CHEMICAL TREATMENT

Scope

- Understand refinery constraints
- Realize trade-off between economic and physical considerations

Chemical Treating

- A tool to deal with process limitations
- An alternative to processing
- Sometimes the only route

CHEMICAL TREATING

Definition

- Addition of small amounts of chemical
- To improve or provide certain properties
- Remains in the fuel

WHY THE NEED FOR FUELS TREATING

- To augment properties of fuels for their intended purpose
- To improve deficiencies in as produced process streams
- More cost effective than process route
- The only remedy available

FUEL TREATING ADDITIVES

Fuels

- Gasoline
- Diesel fuel
- Jet fuel

Aspects of Fuel

- Origin
- Properties
- Deficiencies
- Remedies

ENGINEERING DESIGN SEMINAR

SEPTEMBER 6, 1994 – NOVEMBER 11, 1994

PROCESS ADDITIVES

by. Mr. Nile D. Cable

CORROSION & FOULING PREVENTION

Corrosion Prevention

- Types of Corrosion
- Chemistry of Corrosion – Crude Unit Chloride Control
 - Contaminants
 - Process Variables
 - Surface

Fouling Prevention

- Types of Fouling
- Chemistry of Fouling
 - Contaminants
 - Process Conditions
 - Surface

Wrap Up

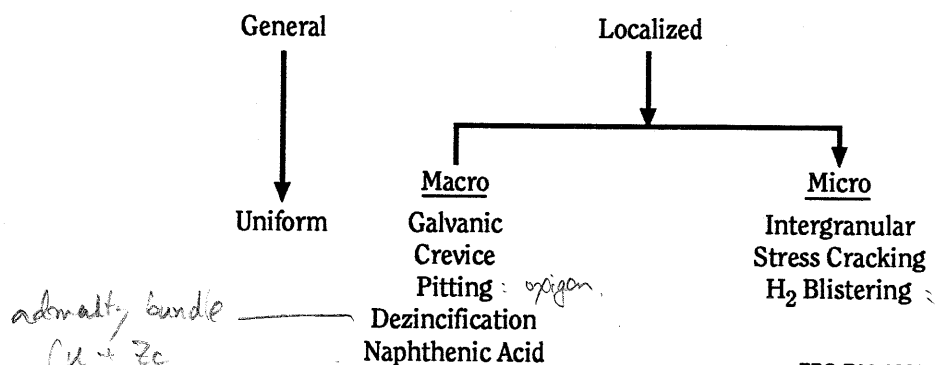
TYPICAL PROBLEM AREAS

In the Refinery

UNIT	CORROSION	FOULING
Crude Distillation	Main Column Overhead Stabilizer Overhead	Preheat Exchangers
Vacuum Distillation	Overhead System	
Visbreaking	Flash Fractionator Overhead Stabilizer Overhead	
Coking	Fractionator Overhead	
Hydroprocessing	Stripper Overhead	Preheat Exchangers Compressors
FCC <i>not different working</i>	Main Column Overhead Stripper Overhead Debutanizer Overhead	Gas Con. Compressors Slurry Oil Area
Reforming <i>Catalyst Chloride</i>	Stabilizer Overhead <i>swab ① continuous use</i>	Stabilizer Column Condenser Separator Recycle Compressors
Polymerization	Debutanizer Overhead	Fractionation Reboiler

*Acid type catalyst + olefins → polymers.
Gums, sediments*

Types of Corrosion



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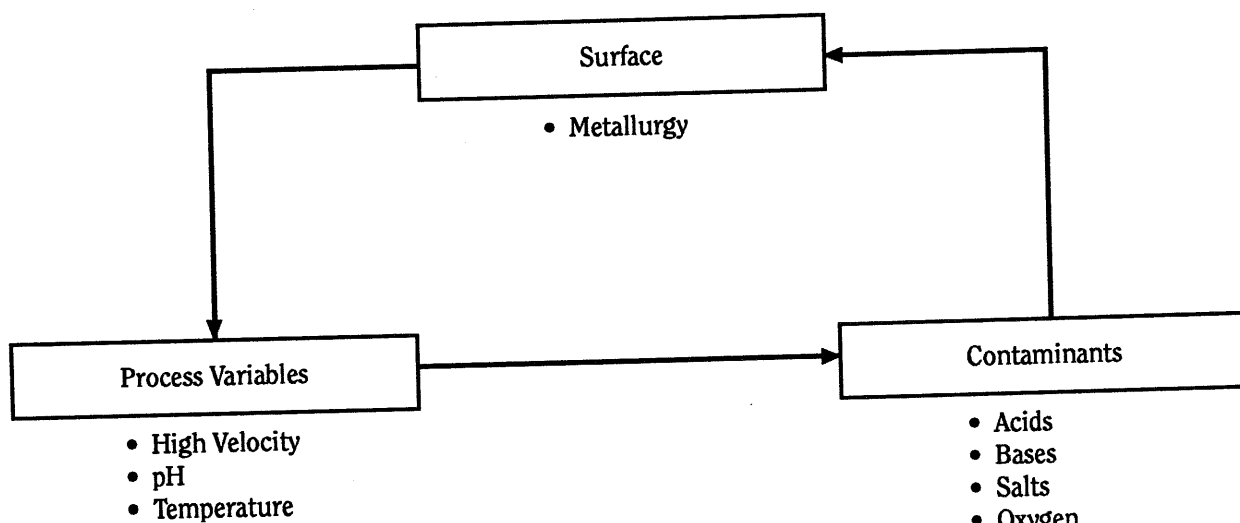
Polysulfide :

*Water in sludge of
Ammonium Sulfide*

CORROSION PREVENTION

- Chemistry of Corrosion
- Control Techniques
- Crude Unit Chloride Control

Chemistry of Corrosion



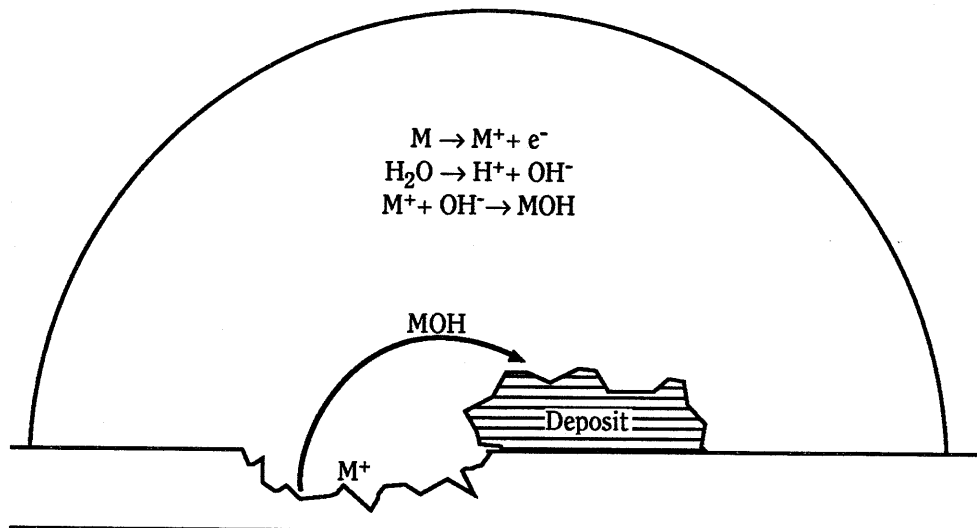
UOP: Velocity ^{Guide} max
20 ft/sec ← 25 ft/sec
Corrosion

- Acids
- Bases
- Salts
- Oxygen
- Water
- Sulfur = H₂S, RSH, S, SO₂

EDS-R00-0621

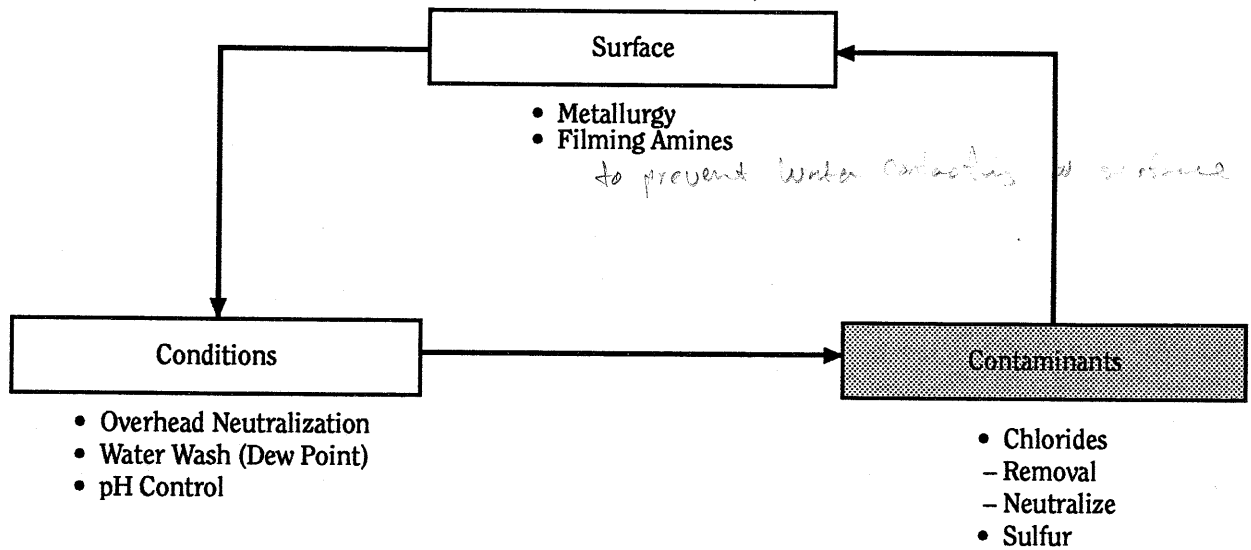
pH.
Ammonium Sulfate from
Feedwater

Corrosion Mechanism Electrolytic Cell



EDS-R00-0622

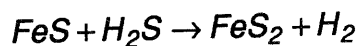
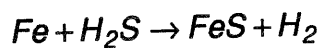
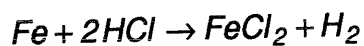
Chloride Control Techniques



EDS-R00-0623a

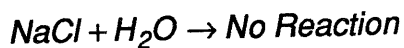
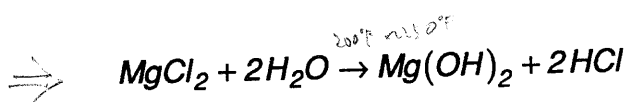
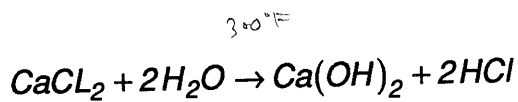
CHLORIDE & SULFUR ATTACK

Common Mechanisms



CHLORIDE CONTAMINATION

1. Inorganic Salt



Desalting
to remove salts

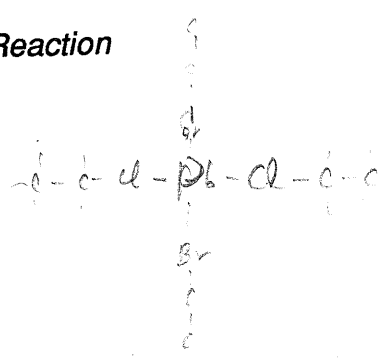
2. Organic Salt

Production Fields

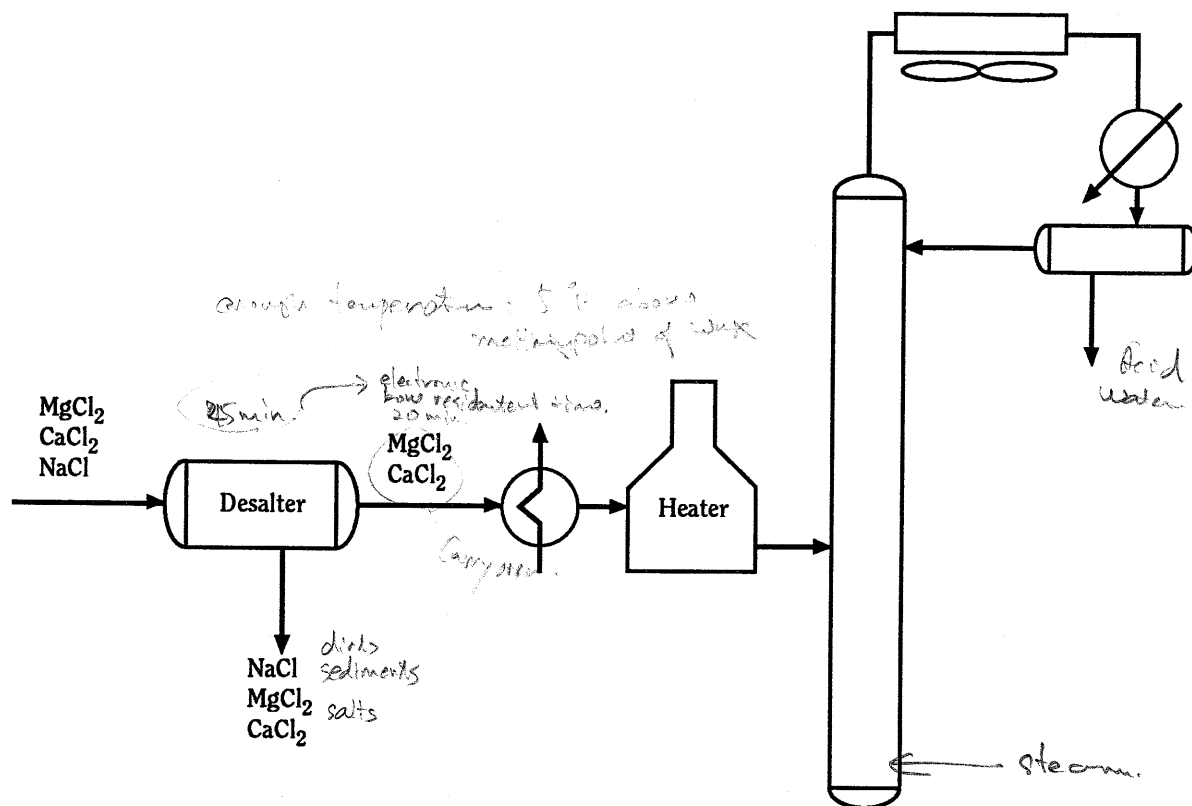
Process Requirements

Reprocessing

→ Decomposition to HCl

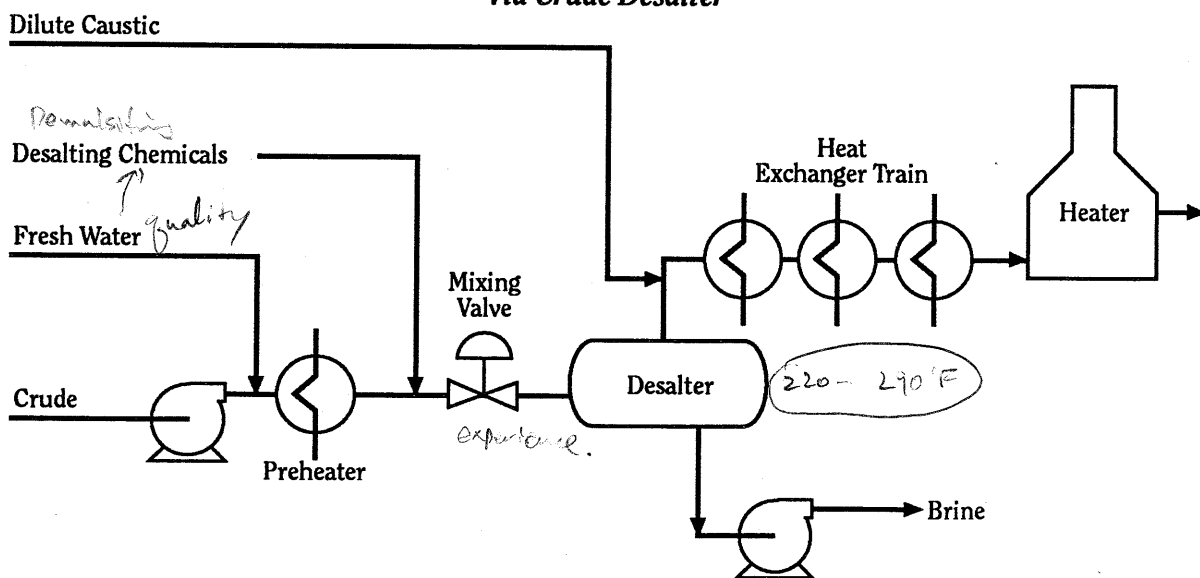


Crude Unit Corrosion Prevention



EDS-R00-0624

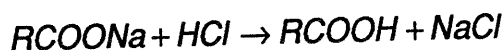
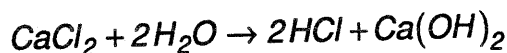
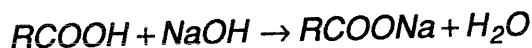
Chloride Removal Via Crude Desalter



EDS-R00-0625

CHLORIDE NEUTRALIZATION

Caustic Injection



CAUSTIC INJECTION CAUTIONS

Furnace Tube Embrittlement

Foaming : excess caustic $\rightarrow$ colour change.

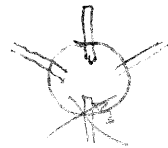
Exchanger Deposits

Sodium Carryover

CAUSTIC INJECTION GUIDELINES

- Use fresh dilute aqueous NaOH (2-3 wt pct NaOH).
- Inject caustic through a monel quill extended into the pipe one-third of the pipe diameter.
- Rate of injection is not to exceed 4 lb of NaOH per 1000 bbls.
- Inject caustic into the crude stream immediately after the desalter. This assures sufficient mixing before contacting furnace tubes.
- Caustic should not be injected into crude over 300 °F.

stress relieve
and Ca, Mg



*NaOH is added thru
HCl is added thru*

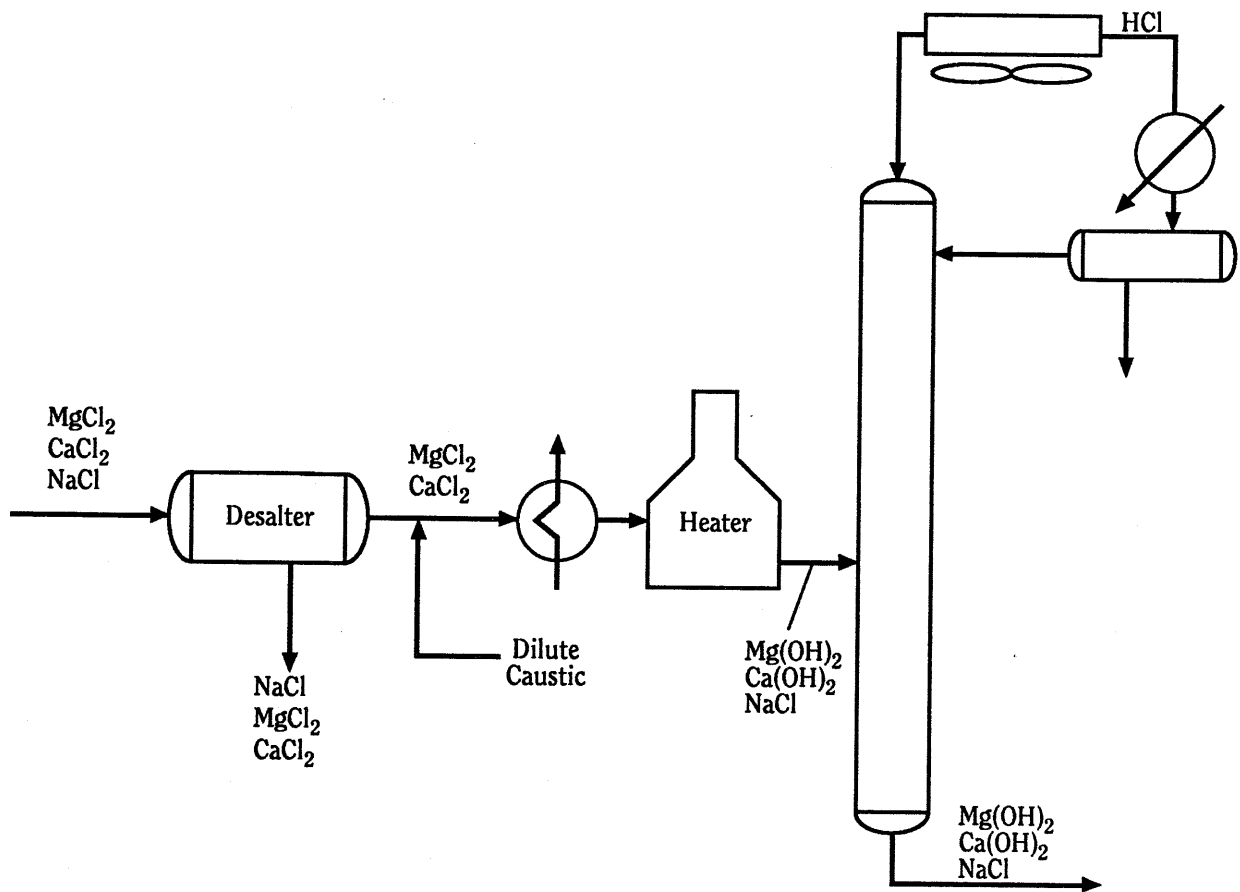
- Caustic should be injected as far upstream of the pumps, control valves, and exchangers as possible (2 meters minimum).
- Caustic injection is meant to augment efficient desalter operation.

GOAL

- 1) Desalter to be operated efficiently
- 2) Caustic injection
- 3) Monitoring: Na , K , NH_4OH , SC-C-642

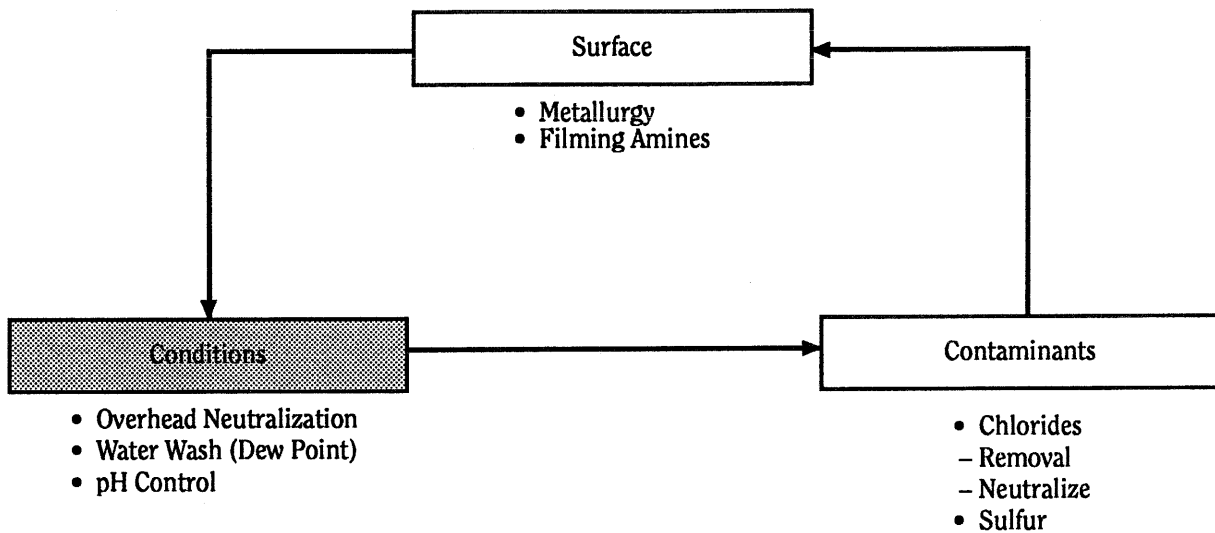
Salt Content in Desalted Crude Must Be Less Than 7 ppm (2 PTB).

**Crude Unit Chloride
Protection**



EDS-R00-0626

Chloride Control Techniques

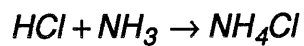


EDS-R00-0623b

OVERHEAD NEUTRALIZATION

Water Dew Point

- With Ammonia



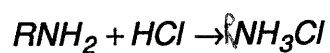
- Why Ammonia?

Inexpensive

Not oil soluble

Produced inorganic salts

- With Neutralizing Amine



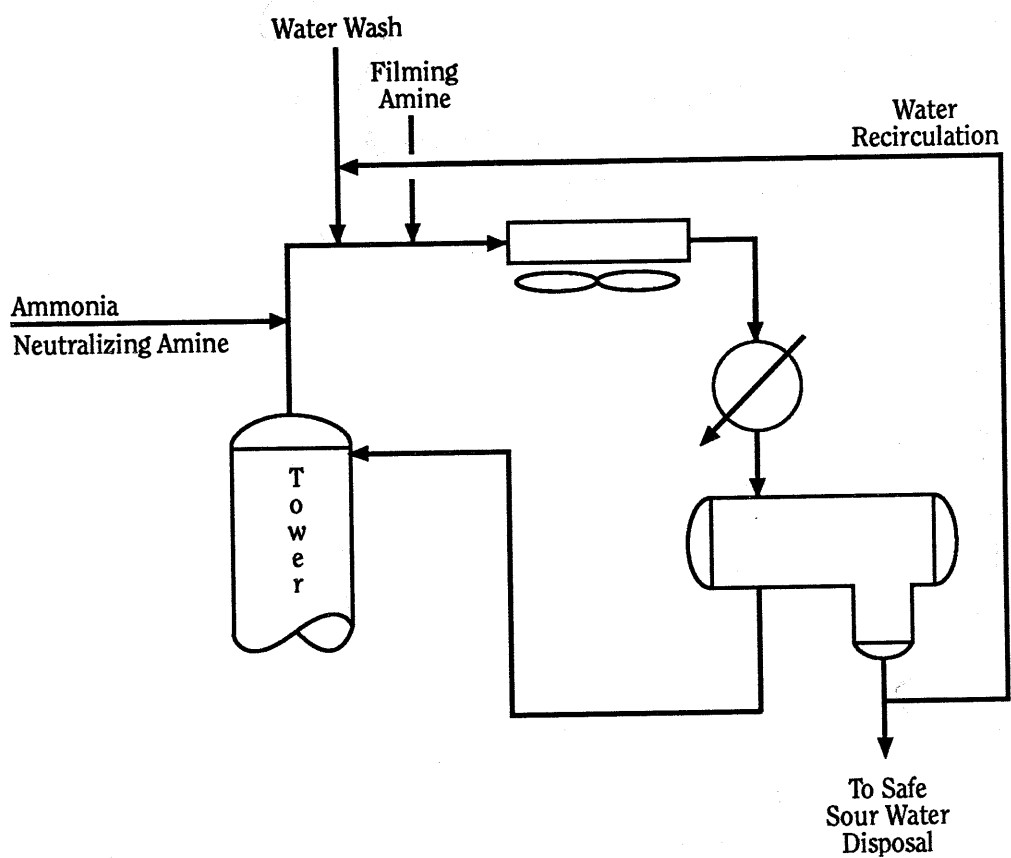
– Why Neutralizing Amine?

Ease of handling

Worker convenience

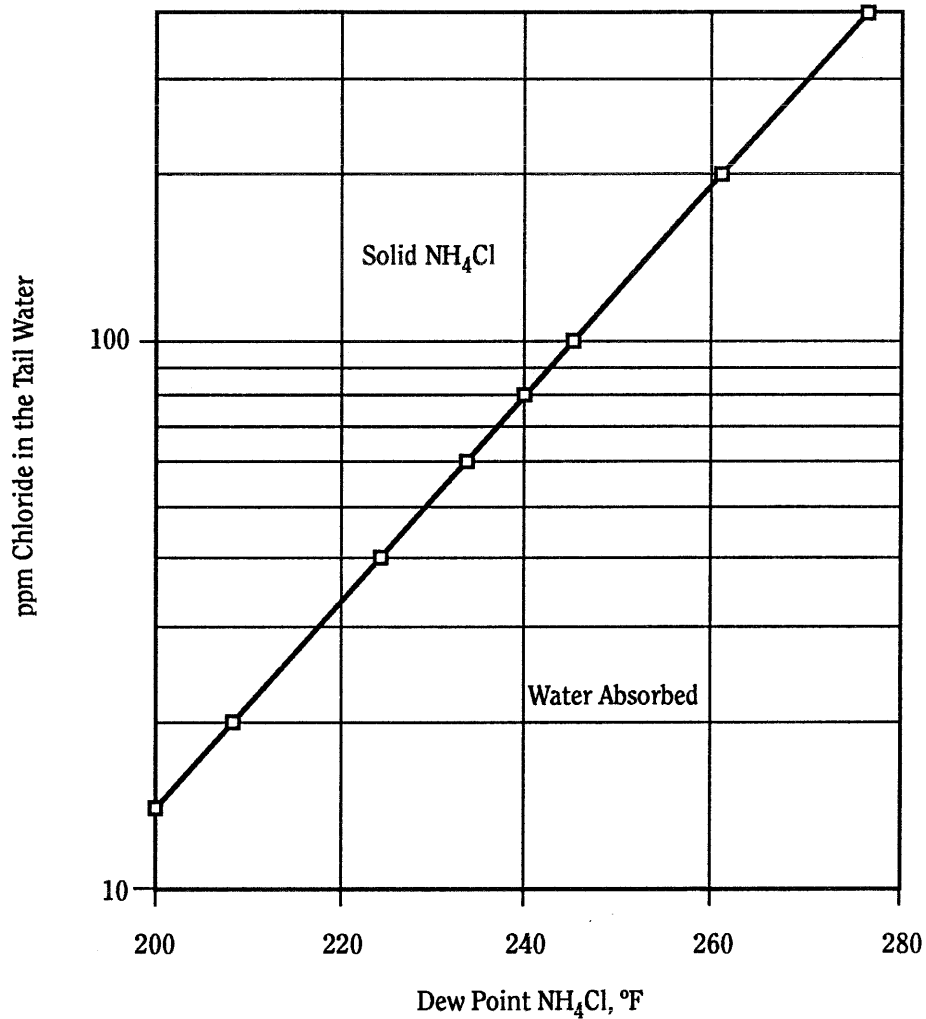


*Corrosion Control System
Neutralizing & Filming Amines*



EDS-R00-0627

Ammonium Chloride Deposition



EDS-R00-0628

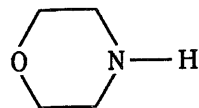
WASH WATER QUALITY

PROPERTY	SPECIFICATION
pH	5.5 – 7.5
Total Hardness	< 50 ppm
Total HCO_3^- and CO_3^{2-}	< 50 ppm
Ammonia (NH_4HS)	< 100 ppm
Chloride	< 2000 ppm
Sulfate	< 200 ppm
Oxygen	< 1 ppm

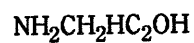
Case

Organic Neutralizers

Morpholine



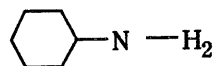
Ethanol Amine



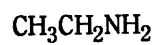
Di-Ethyl Amine



Cyclohexylamine

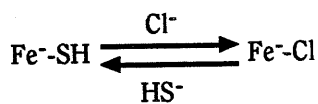


Ethylamine



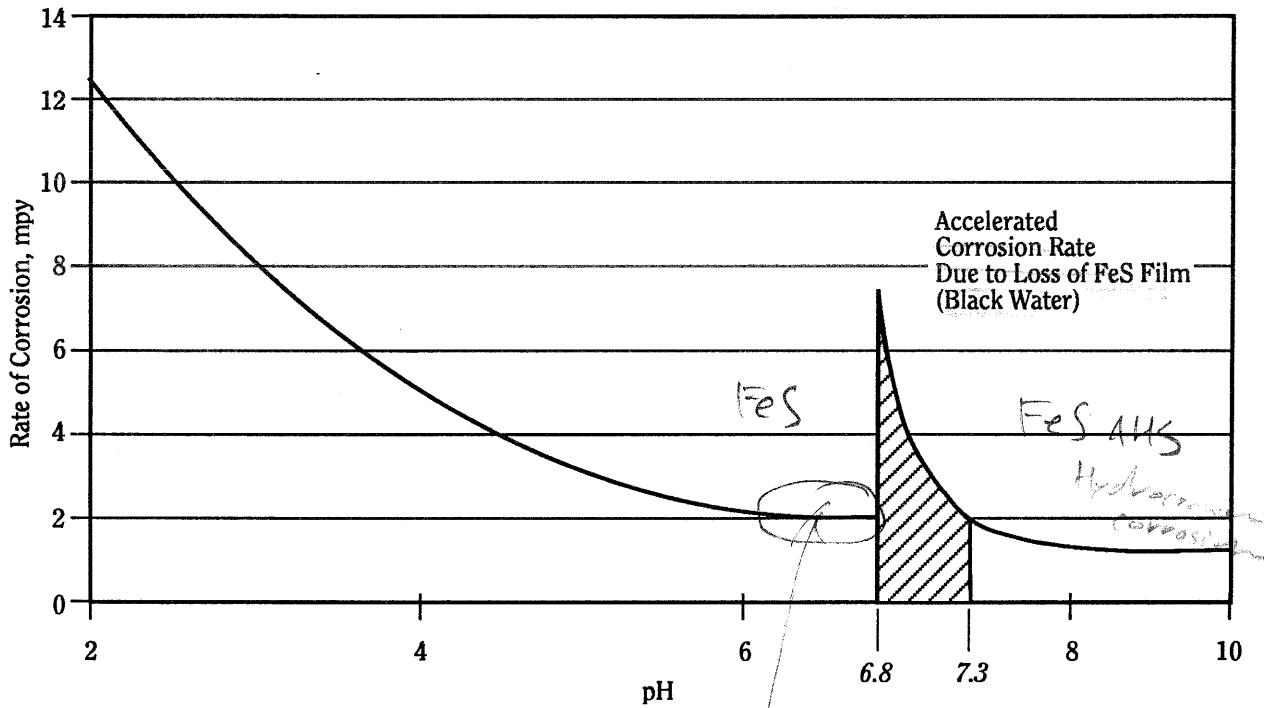
EDS-R00-0629

Process Control Competing Mechanism



EDS-R00-0630

pH Effect of Sulfide Corrosion



Note: Occurs in Crude Tower Overhead Only

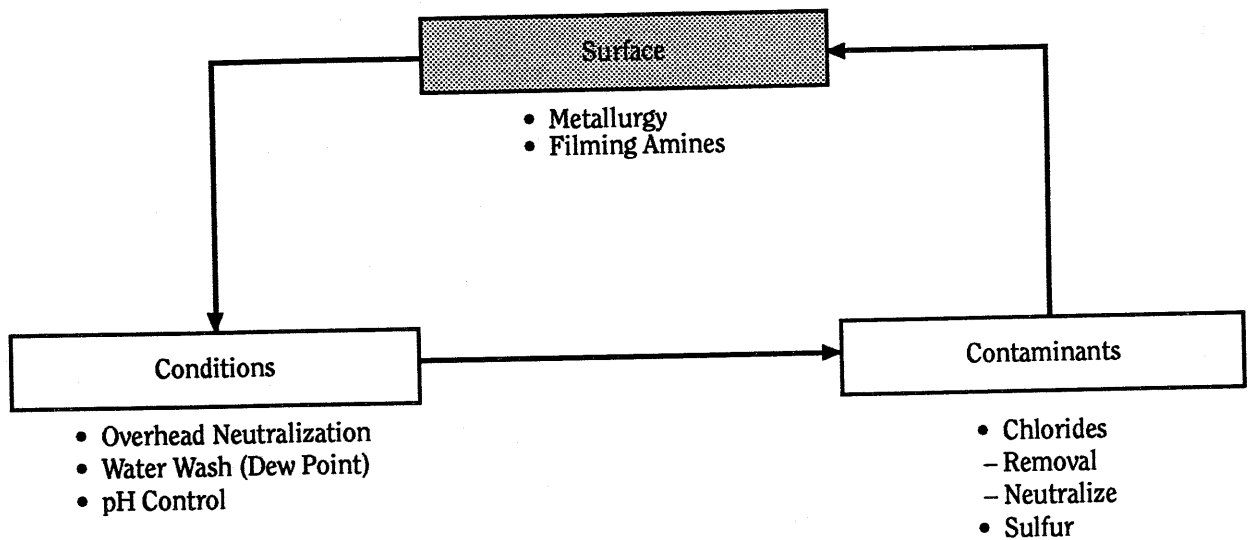
EDS-R00-0631

pH Control Target

pH CONTROL OBJECTIVE

- Provide a controlled non-corrosive environment.
- Maximize the effectiveness of the filming amine.

Chloride Control Techniques



EDS-R00-0623c

FILMING AMINES

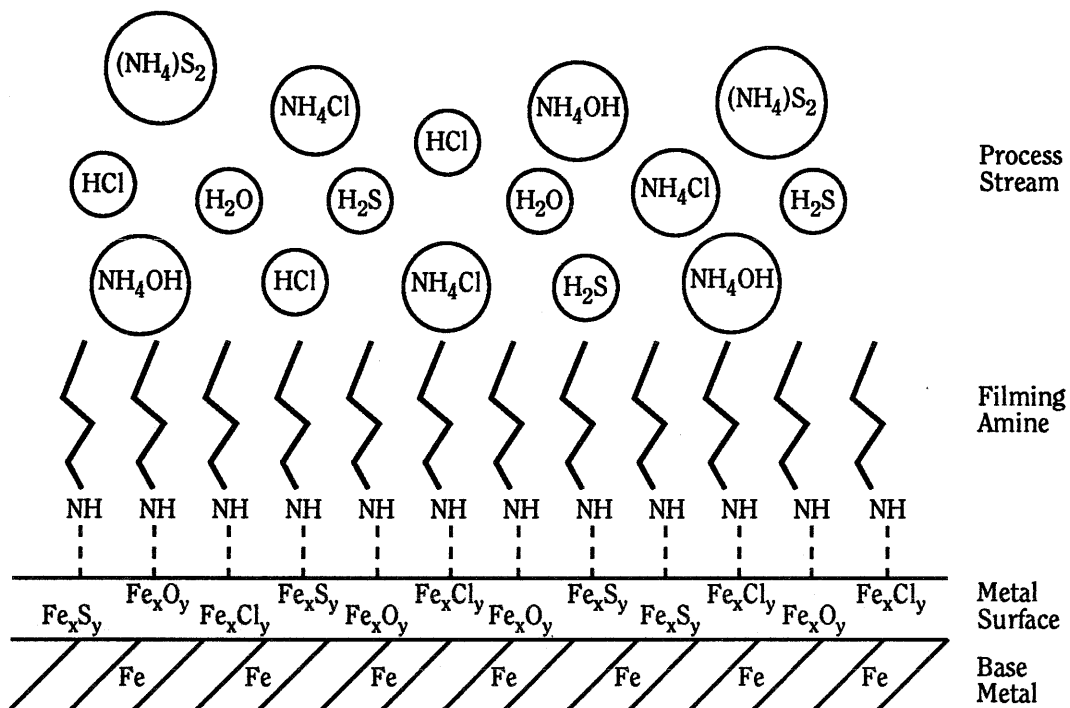
Function

Filming amines provide a monomolecular layer serving as a barrier between the metal surface and the corrosive environment.

Limitations

- Decomposition temperature
- pH range
- Process stream velocity

Film Forming Theory



EDS-R00-0632

FILMING AMINE SELECTION

Type of Chemical

Solubility in hydrocarbon

Surfactancy

Reactivity in environment

Affects on downstream equipment

Performance

Cost effectiveness (dosage x price)

Injection system

Other

Handling & toxicity

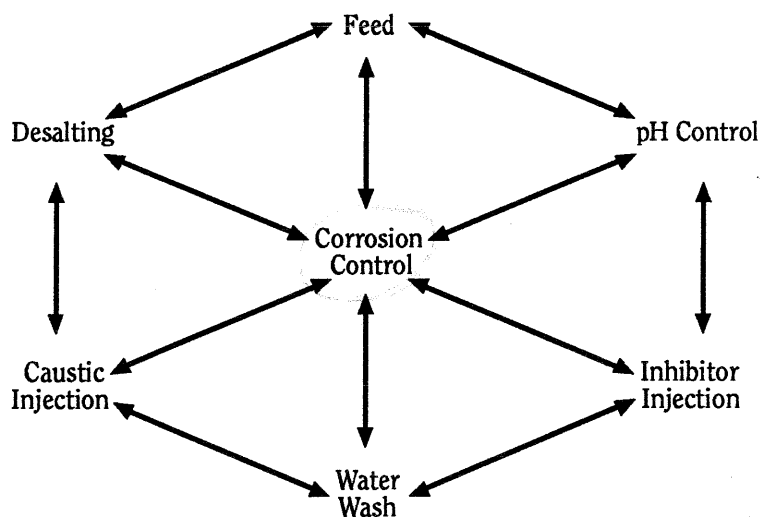
Technical and product support

Reputation of supplier

FILMING AMINE ACTIVITY

AMINE CLASS	FILM TENACITY	RESISTANCE TO HCl AND H ₂ S	WATER REACTIVITY	EFFECT OF pH	PROBLEMS
Ethoxylated	Poor	Some	Depends on degree of ethoxylation	Moderate	High dosage
Primary	Poor	Low	Salts emulsify	High	Carryover and emulsions
Secondary	Good	Very good	Salts emulsify	Moderate	Reactivity and emulsions
Neutralized acids	Fair	Very good	Low	Moderate	Poor oil solubility
Neutralized dimer acids	Excellent	Very good	Low	Moderate	Potential emulsions
Imidazolines	Excellent	Very good	Low	Moderate	Potential emulsions
Amides	Very good	Very good	Very low	Low	Emulsions and solubility
Phosphate esters	Excellent	Very good	Low	Low	Decomposition temperature

Relationship of Corrosion Control Techniques



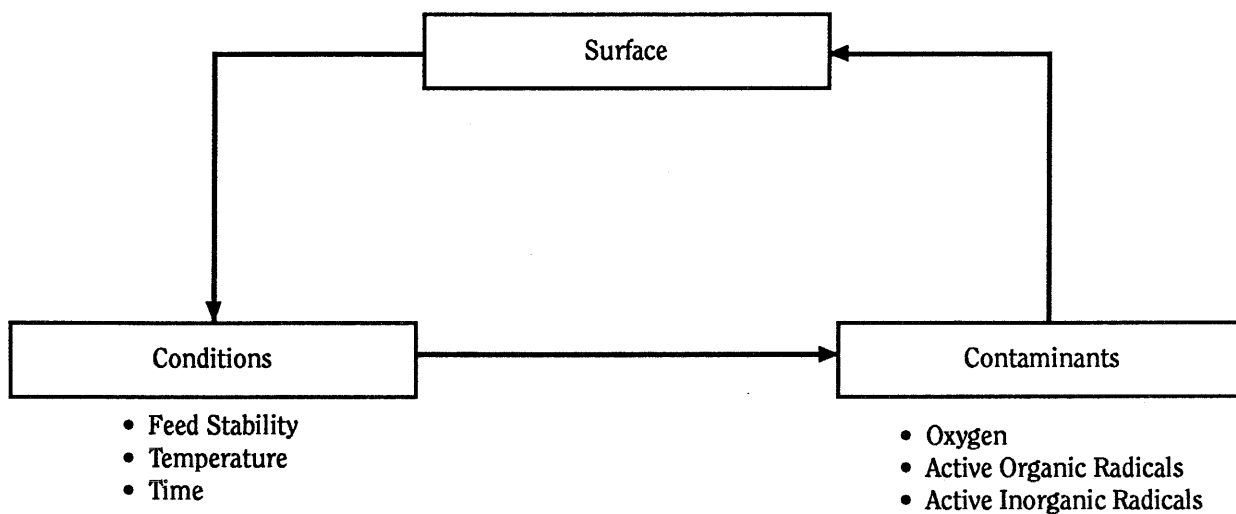
EDS-R00-0633

CORROSION AND FOULING PREVENTION

TYPES OF FOULING

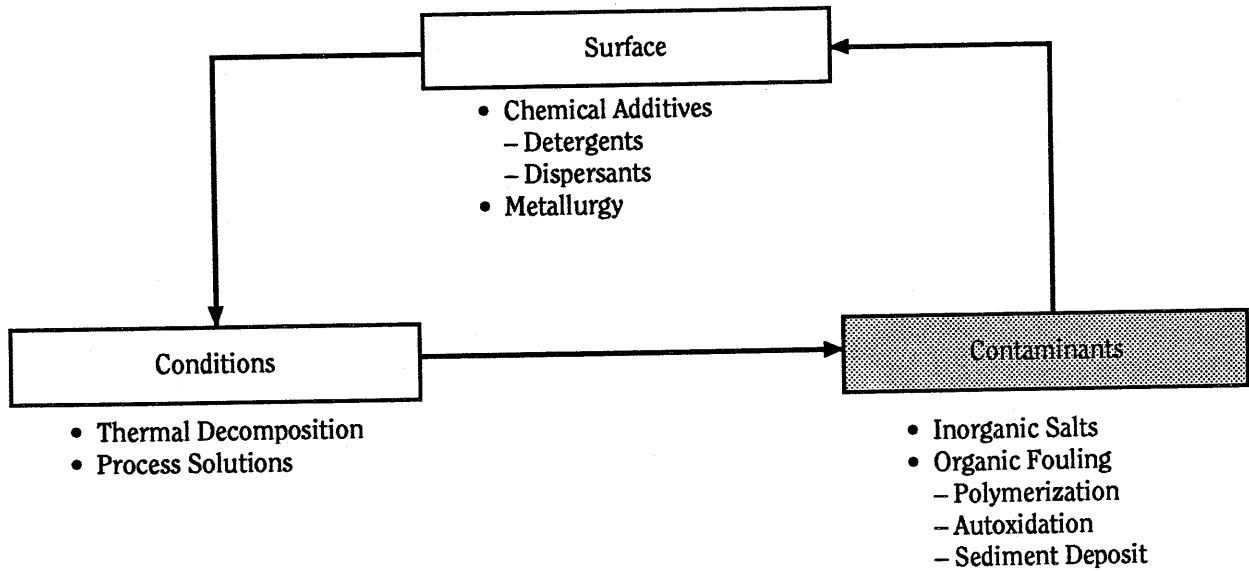
INORGANIC	ORGANIC
Salts Corrosion Products	Gums Sludges Waxes Varnishes

Chemistry of Fouling



EDS-R00-0634

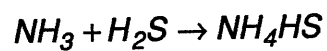
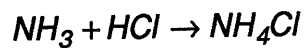
Chemistry of Fouling



EDS-R00-0635

INORGANIC SALT

Deposition



Their accumulation will cause under deposit corrosion.

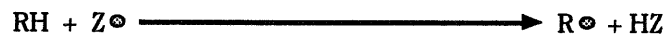
ORGANIC FOULING

Often Involves a Stream Degradation Mechanism

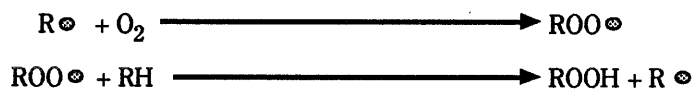
- Autoxidation
- Polymerization

Autoxidation

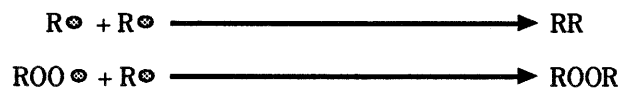
Initiation:



Chain Propagation:



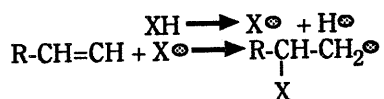
Termination:



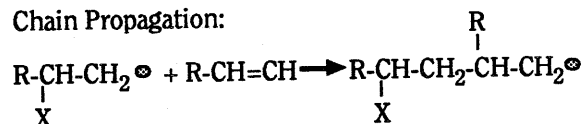
EDS-R00-0636

Polymerization

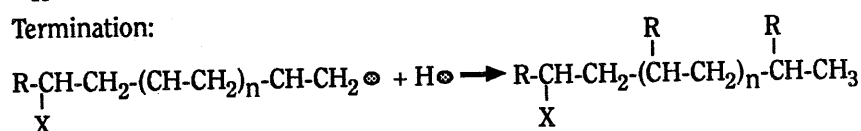
Initiation:



Chain Propagation:



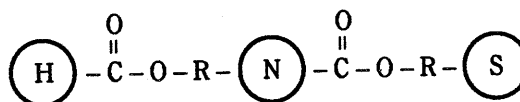
Termination:



EDS-R00-0637

Esterification

Sediment Molecule



Where:

H: Hydrocarbons

Benzenes
Diphenyls
Naphthalenes
Tetralines
Tricyclic Aromatics

N: Nitrogen Compounds

Carbazoles
Indoles
Pyridines
Pyrroles
Quinolines

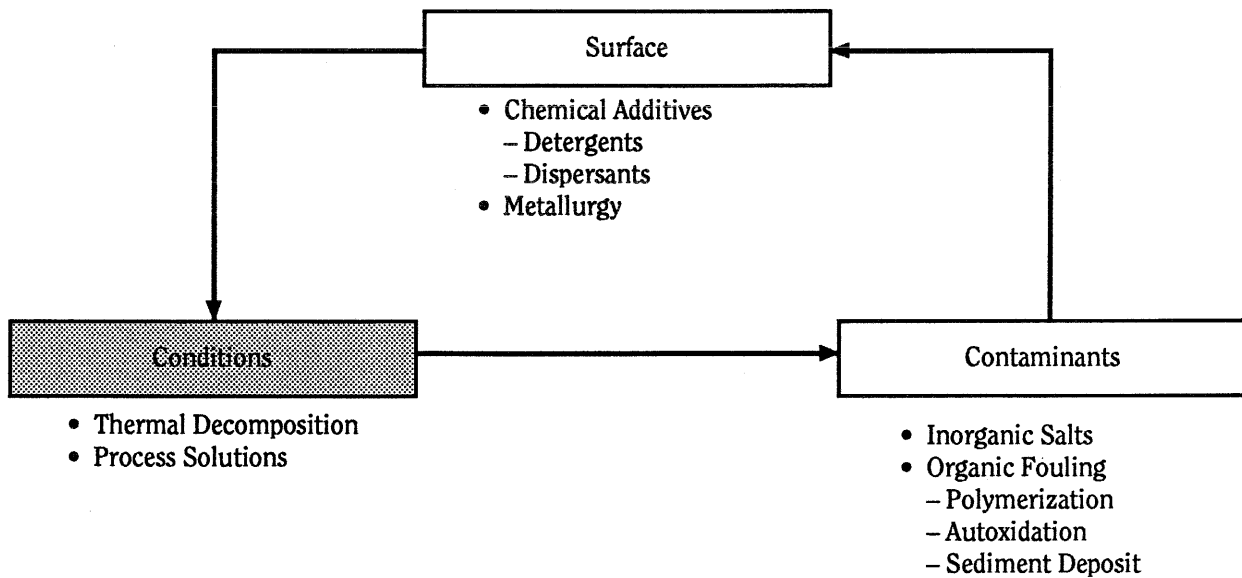
S: Sulfur Compounds

Thiophenes
Cyclic Sulfides

Possible Combinations:
HNH HNS NHH NSH NNN

EDS-R00-0638

Chemistry of Fouling



EDS-R00-0639

THERMAL DECOMPOSITION

This Takes Place Under Coking Conditions.

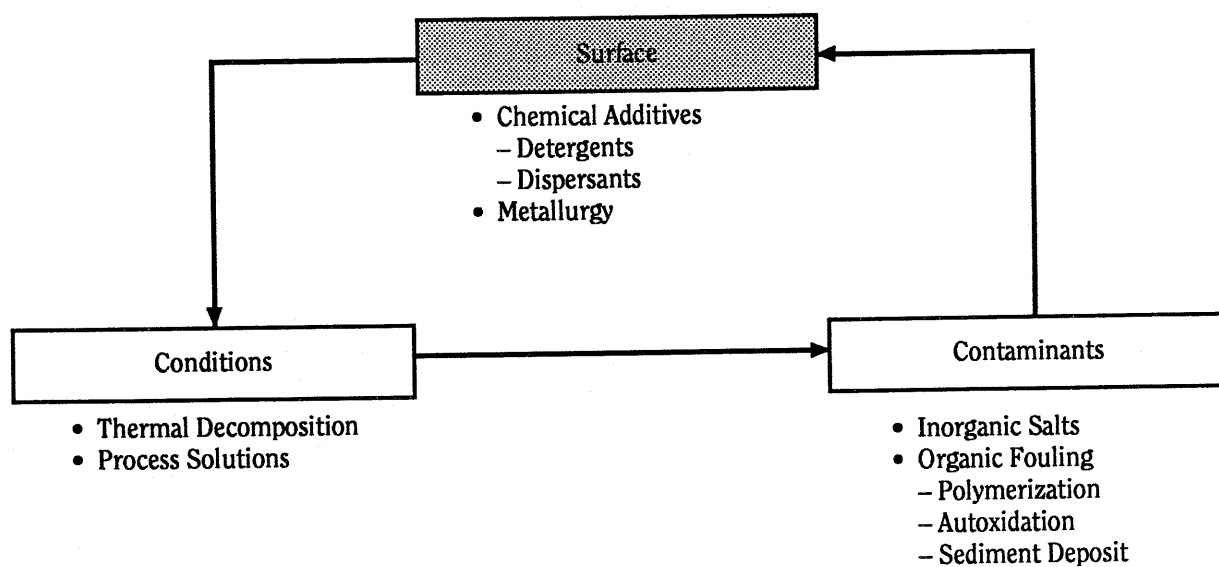
- Organic Deposits
- High Temperatures

PROCESS SOLUTIONS

<i>Pre</i> ACTIVE	REACTIVE
Gas Blanketing	Gas Stripping
Handling/Blending	Prefractionation
Sourcing	Rerun
Desalting	Water Wash
Design Metallurge	Filtration

– Chemical Additives –

Chemistry of Fouling



EDS-R00-0640

CHEMICAL ADDITIVES

Optimize Unit Performance

	<i>PRO</i> Active	Reactive
Inorganic	Desalting Corrosion Control	Water Wash
Organic	Antioxidant Stabilizers Metal Deactivators	Antifoulant

Functions

- Prevent Stream Degradation

Antioxidant

Stabilizer

- Clean Metal Surface

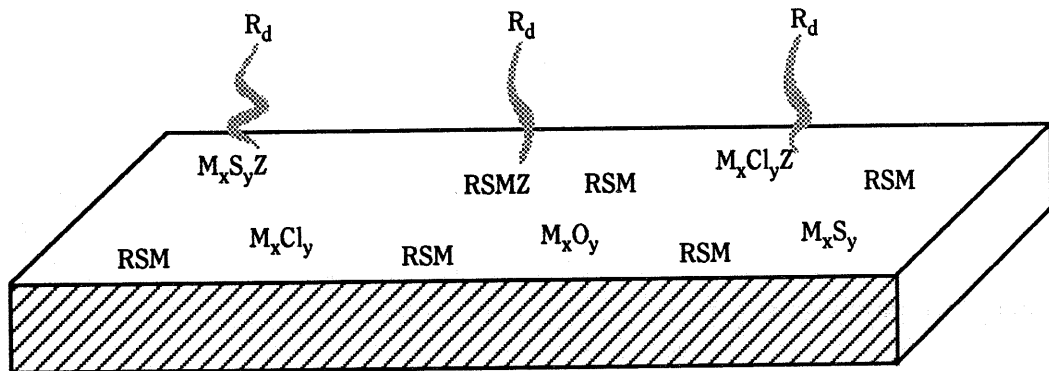
Detergency

Film forming

- Disperse Sediments

Dispersion

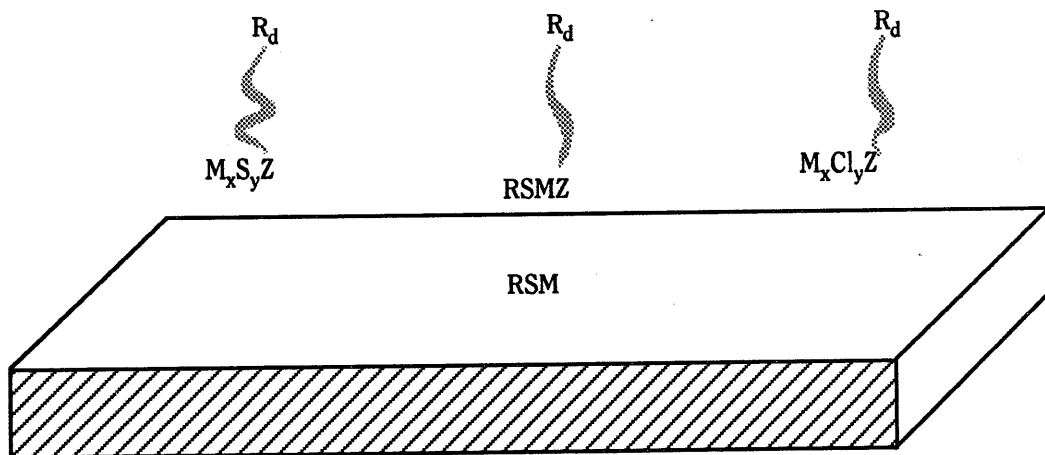
Detergency



$R_d Z$ Is the Detergent
 Z Surface Active End of Detergent
 R_d Hydrocarbon Soluble End of Detergent

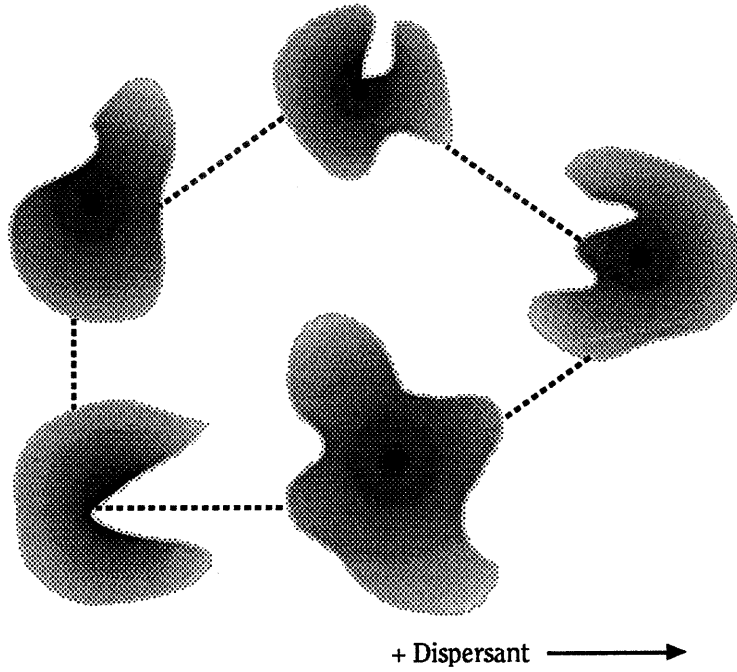
EDS-R00-0641

Detergency



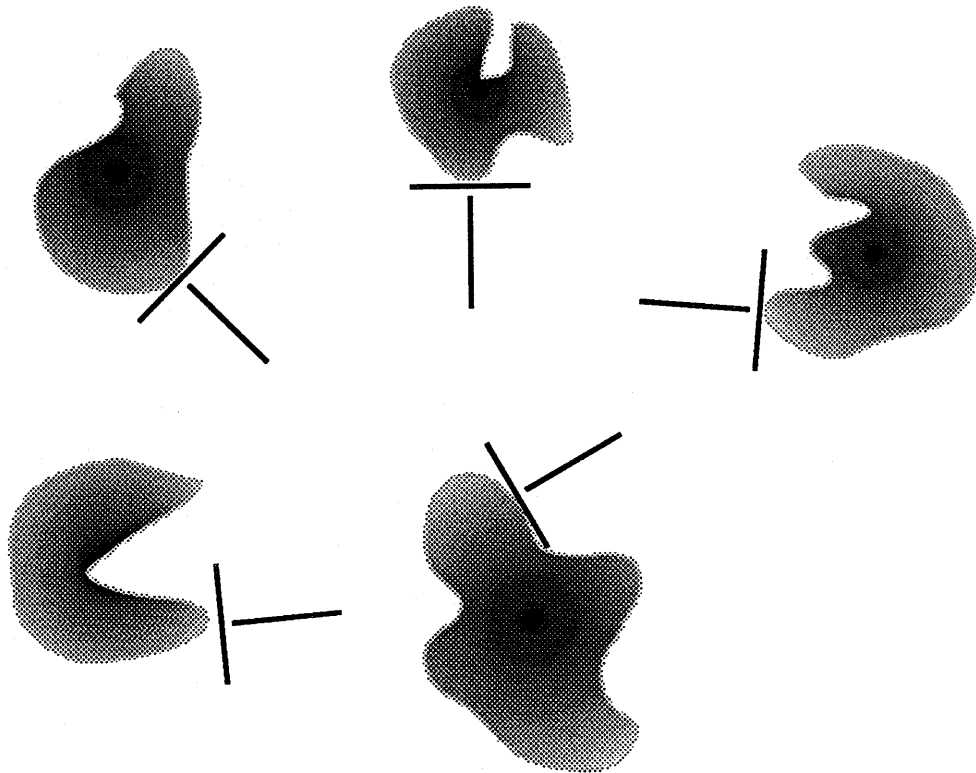
EDS-R00-0642

Dispersion
Agglomerate – Ionic Bound



EDS-R00-0643

*Dispersion
Dispersant Reacts to
Break Up Agglomerate.*



EDS-R00-0644

METALLURGY

Smoothness

Different metallurgies have different surface roughness

High surface roughness can increase the occurrence of fouling by trapping sediment



EDS-R00-0645

DETERGENTS are primary movers of materials!

They can cause downstream fouling of a worse nature than the existing problem.



EDS-R00-0646

CAUTION!

Some additives can be poisons to downstream catalytic units.

ROLE OF CHEMICALS

Modify Contaminants

- Neutralize Corrodants
- Retard Fouling
- Disperse Sediments

Change Conditions

- Alter Corrosion/Fouling Mechanism

Modify Surface Condition

- Provide Protective Barrier
- Clean Surface Contaminants

CONSIDER THE FOLLOWING . . .

- Chemical additives may affect other areas.
- Their performance must be continually monitored for optimum benefits.
- Their economic feasibility is justified by the increase in equipment life which translates into savings.
- The design engineer's involvement in a corrosion or fouling program is imperative to its success.

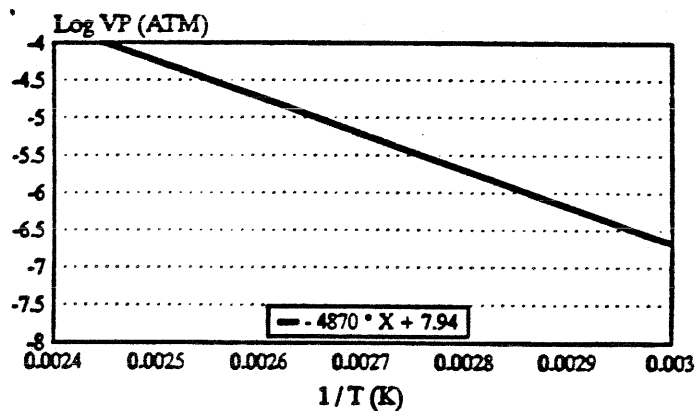


Figure 1
Equilibrium Vapor Pressure Function
of NH_4Cl

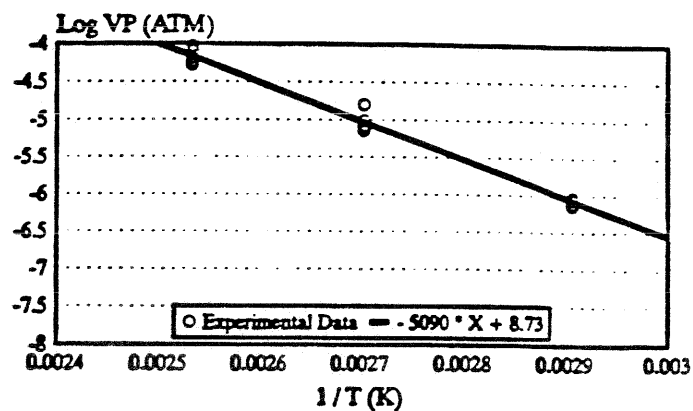


Figure 2
Equilibrium Vapor Pressure Function of
Amine E Hydrochloride Salt

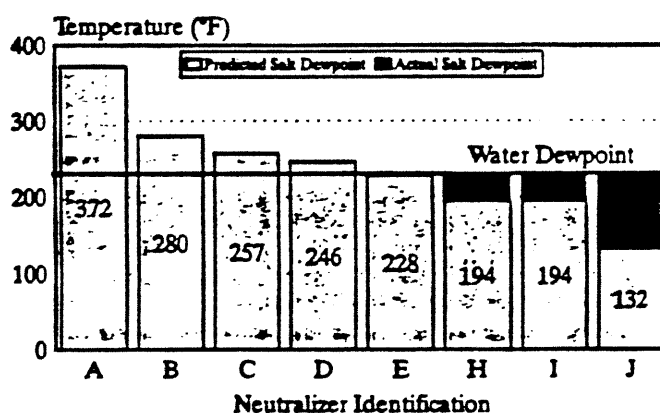


Figure 3
Amine Hydrochloride Salt Dewpoints
for Gulf Coast Refinery

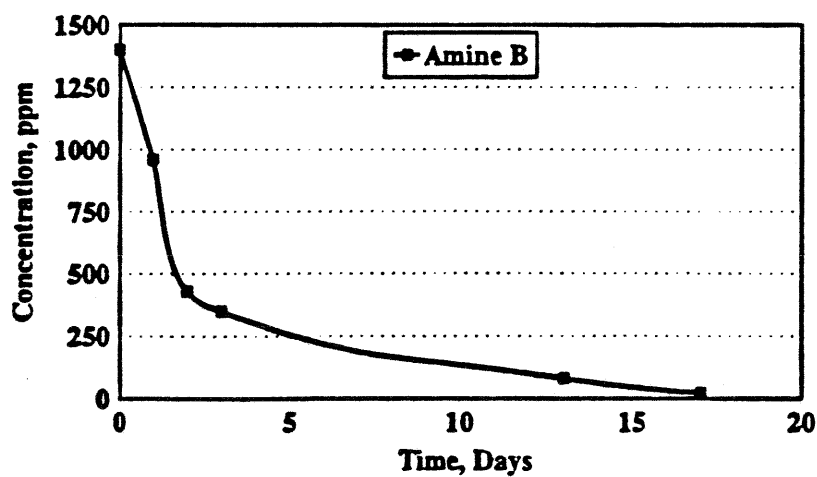


Figure 4
Product Change at Midwestern Refinery

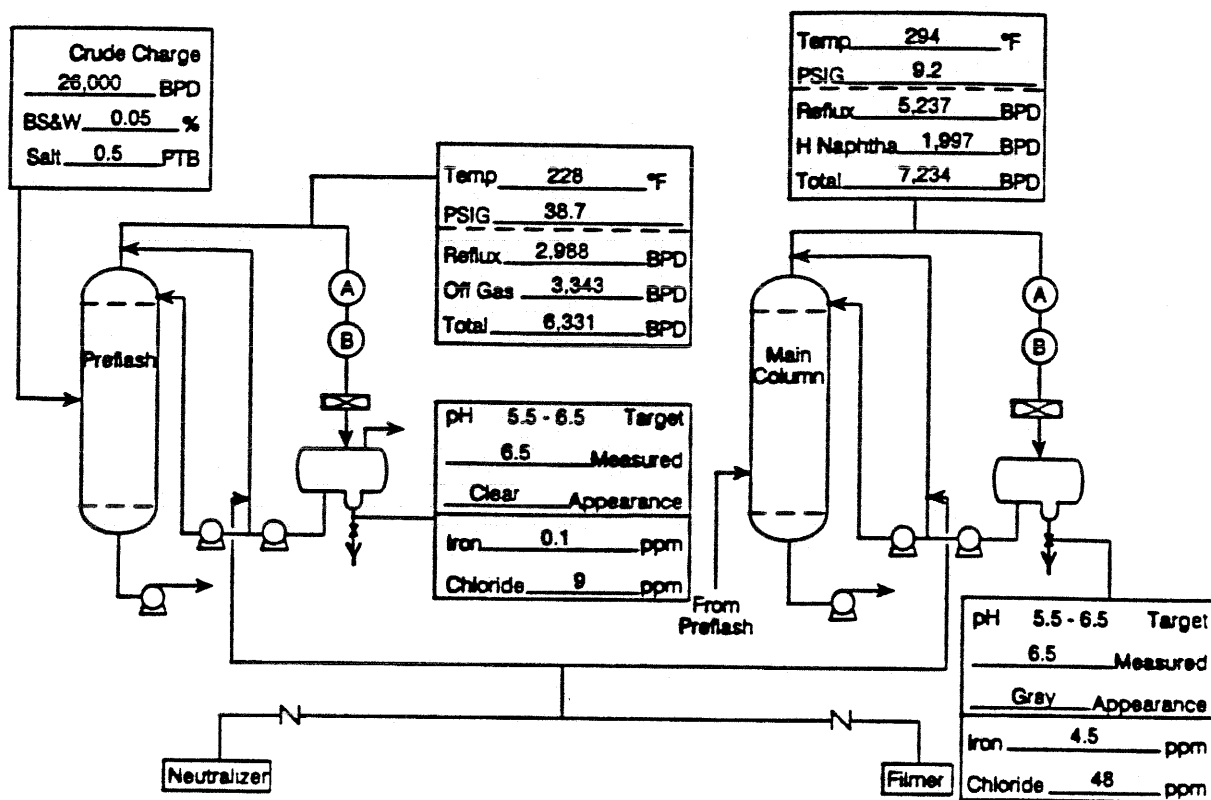


Figure 5
 Schematic of Northwestern Refinery
 Crude Unit

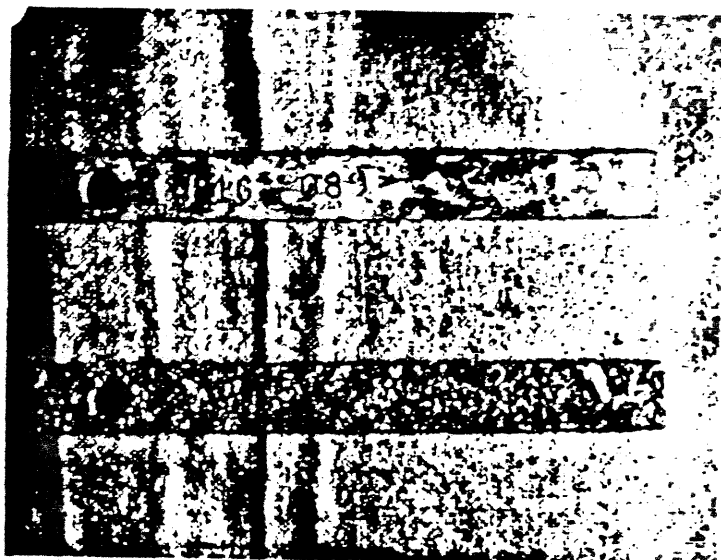


Figure 6: Deposits on Corrosion
 Coupons, Exposed Between
 Overhead Exchangers at
 Northwestern Refinery Crude
 Unit (Top: Amine F, Bottom:
 Amines D and E)

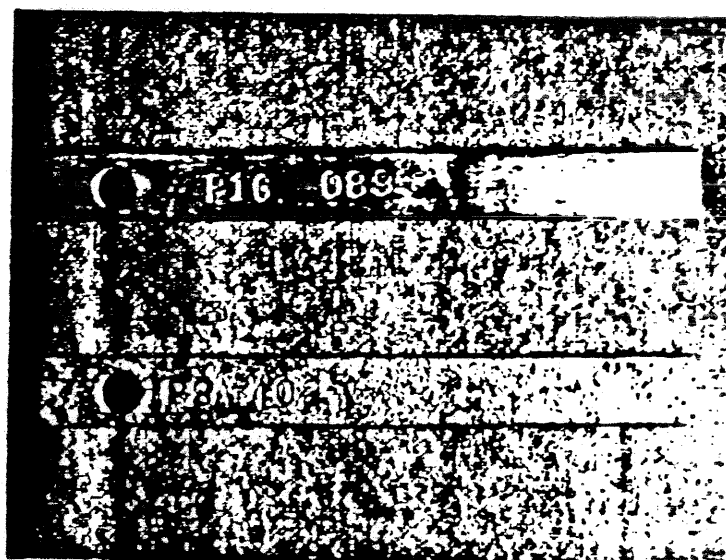
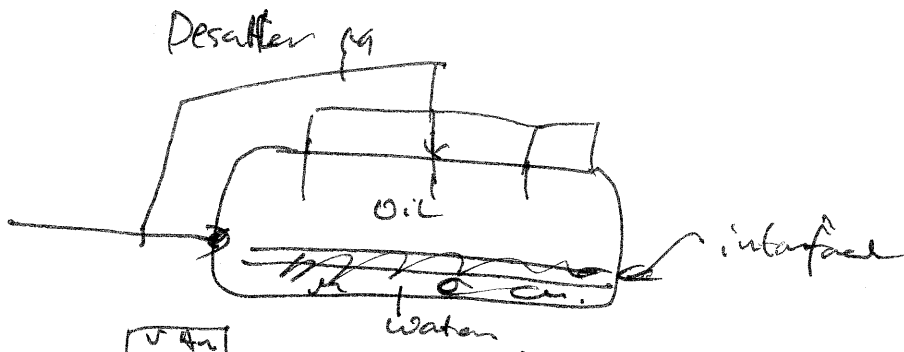


Figure 7: Cleaned Corrosion
 Coupons, Exposed Between
 Overhead Exchangers at
 Northwestern Refinery Crude
 Unit (Top: Amine F, Bottom:
 Amines D and E)

PROCESS ADDITIVES

by Mr. Mike D. Cobb



each other should be equal. volt and ampere.

Water selection qualities is effect on selection of chemicals.

NaS : spent caustic. Not oil soluble.

NaOH

R- cooma.

Netamz : water soluble.

UOP - REFINING CHEMICALS DEPARTMENT FAX MESSAGE

ATTENTION: André Claus DATE: March 30, 1994
COMPANY: Grace Dearborn LOCATION: Antwerpen
FROM: Nile D. Coble PHONE: 708/391-3002
SUBJECT: Neutralizing Amines
FAX NO.: (32) 3-830 42 83

Per your request to Alan Cepla, I will try to present some information on neutralizing amines. I will not be able to answer all your questions but I will try.

The shortest chain inorganic nitrogen neutralizer is ammonia. Ammonia will neutralize chloride ion in the gas phase or hydrochloric acid in the aqueous phase. A substitute for ammonia was used to get around UOP patents on the use of ammonia, filming amine and water wash. The first application in 1960 of neutralizing amine was at The Standard Oil Company (Ohio) in Lima, Ohio (now known as BP Oil). Nalco used morpholine from the boiler house to use the water wash technique in the presence of a filming amine. The neutralizer was successful and very profitable.

There have been many technical papers written on the subject of neutralizing amines and most were presented at NACE. A number of papers which indicate that they work in the overhead of a tower, they work in the water condensing area, and some are not fouling. However, no neutralizing amine so far presented in the literature has been tested in the presence of hydrogen sulfide. All work, with water to hydrocarbon phase test ratios, was tested in sweet naphtha hydrocarbons on boiler water test equipment. If you find a sulfur free refinery crude unit, the test work will be valid.

UOP believes that the neutralizer as supplied by the chemical vender should be properly tested for the potential market. There are a great many varieties in the market place. Betz at Corrosion/94 presented a paper on their improved neutralizers. They list 5 products that indicate fouling potential. Betz also lists some of the Betz products that do not present salt fouling in the crude unit overhead. Unfortunately these products have hydrocarbon solubility so the amine chlorides and amine sulfides stay in the hydrocarbon phase and go down stream to other process

units. They do not harm the crude unit. That is good. They do cut the life of process catalyst down stream and that is very expensive. Betz did not test the product in the presence of sulfides and do not know the solubility of the amine sulfide salt at crude unit process overhead conditions. They have not done their homework.

You requested information on the condensing rate of the chloride salts in water/ hydrocarbon processes. The published information is useless as it does not address the process parameters.

I have test data by a major Oil Company Research Center pilot plant. Using a simulated crude unit with a saturated hydrogen sulfide vapor stream, as found in most crude units, they could not get any of over a dozen neutralizing amines to go above 8 pH. They went to extreme overdoses of additive to see what would happen. They found that the amine sulfide was oil soluble and would not foul the system. Another item noticed was that the pH was measured in the water phase and the amine sulfide was in the hydrocarbon phase. Under the conditions with high hydrogen sulfide levels, pH measurement control to prevent over dosing the additive was almost impossible as the excess amine was not in the water. In one of the Oil Companies Refineries, the excess amine was attacking the monel overhead transfer lines and monel condensing exchangers.

I have observed a test in another Oil Company where ammonia was substituted for neutralizing amine on a mol per mol concentration basis. When the additives were diluted in the day tank to equal molar concentrations, the pH did not change with a constant pump stroke. I feel that neutralizing amines work equally as well as ammonia. They are easier to control due to the more dilute concentration which results in a larger change in pump stroke with chloride change.

The hydrocarbon solubility of amine salts and lack of any test data where sulfides are present do concern us as we have seen a large number of applications where down stream catalyst has been severely deactivated. For this reason UOP has a specification on permissible nitrogen levels of 0.5 ppm in the hydrocarbon before platinum containing catalyst units. If a hydrocarbon soluble neutralizing amine or the hydrocarbon soluble salts of a neutralizing amine are used, it is the responsibility of the supplier to test and monitor the stream for nitrogen.

I am attaching a copy of "Advances in Neutralizing Amine Technology" by J. G. Edmondson and S. E. Lehrer of Betz Process Chemicals. This paper addresses some of your questions. However, they are tested in the absence of sulfur so the work is still not valid. Note table 1 in the paper for salt precipitation index. Also note table 2 and I believe that you will find the additives to have hydrocarbon solubility. Betz has consistently used these types of products. They have also resulted in deactivating a large number of catalyst beds. The additives work very well in the crude unit but the side effects of poor additive control have been deadly downstream.

UOP • DES PLAINES, IL

I regret that my answers are not exactly as you expected. I do feel that you should be aware of the concerns for process applications and the results of miss-application and control of the additives.

After you have reviewed my answers, I will be happy to work with you in your additive applications.

Best regards,

A handwritten signature in cursive script, appearing to read "Nile D. Coble".

Nile D. Coble
Manager Technical Support
Petrochemical and Chemical Products

cc: Phil Malloy
Grace Dearborn
Lake Zurich, IL

Paper No.
514



CORROSION 94

The Annual Conference and Corrosion Show
Sponsored by NACE International

ADVANCES IN NEUTRALIZING AMINE TECHNOLOGY

J. G. Edmondson and S. E. Lehrer
Betz Process Chemicals, Inc.
9669 Grogan's Mill Road
P.O. Box 4300
The Woodlands, TX 77387

ABSTRACT

Corrosion and fouling above the water dewpoint has been reported in many crude unit overheads and on the upper trays of crude towers. Field studies were conducted which show that these problems are commonly caused by deposition of amine and/or ammonia hydrochloride salts. Since these salts can deposit only if their equilibrium vapor pressures are exceeded, salt volatility is a major criterion of neutralizer selection. A survey of the literature indicates that amine salt volatility has not been considered in a quantitative manner until now.

Knudsen effusion measurements have been used to determine equilibrium vapor pressure functions for the hydrochloride salts of five commonly applied neutralizers and ammonia. A spreadsheet was developed to utilize these vapor pressure functions along with crude unit operating conditions to predict salt dewpoints in crude units. To address the needs of crude units where salt deposition is not avoidable with traditional neutralizers, a research program was conducted to develop new neutralizers which form more volatile hydrochloride salts. Case histories are presented which discuss results of field trials with traditional and novel neutralizers.

Keywords: crude unit, neutralizing amine, volatility, salt deposition, water dewpoint, overhead corrosion, test methods

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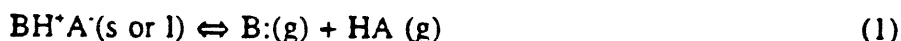
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INTRODUCTION

High corrosion rates, 200 to 500 mpy (5.08 to 12.7 mm/y), have been reported in crude unit overhead systems and on the upper trays of crude towers at temperatures as much as 70 °F (21 °C) above the water dewpoint.⁽¹⁾ Numerous field cases have shown that these problems can be due to the formation of neutralizer salts, including those of ammonia. The primary acid involved in salt formation is hydrochloric acid. The deposition of these neutralizing amine hydrochloride salts has also caused fouling of overhead equipment and the upper trays of crude towers⁽²⁾ resulting in loss of heat transfer efficiency, reduced throughput, and product quality problems.

There are currently several criteria used by specialty chemical companies in selecting neutralizing amines for crude unit applications. These criteria include cost, equivalent weight, base dissociation constant, water dewpoint neutralization efficiency, buffering, volatility, and hydrochloride salt properties. The fact that hydrochloride salt properties are considered important indicates that the neutralizer may react with HCl above the water dewpoint and that salt precipitation is unavoidable in certain systems. The traditional approach towards reducing deposition of the precipitated salts has been to apply neutralizers which form hygroscopic, low melting point hydrochloride salts which are liquid at temperatures above the water dewpoint. These neutralizers are applied based on the theory that liquid salts, formed above the water dewpoint, will be flushed through the system by liquid hydrocarbon and not contribute to fouling. As will be shown in several field studies, this theory is not always borne out in practice.

The sublimation of neutralizer or ammonium salts can be expressed by the following general equation



In the gas phase, dissociation is essentially complete and there is no vapor phase "salt" species. The equilibrium constant for salt formation is given by:

$$K = P_{\text{B}} \cdot P_{\text{HA}} \quad (2)$$

Where P indicates the partial pressure of the appropriate specie.

In addition to HCl, other acids and acid gases exist in crude units, examples include acetic acid, hydrogen sulfide, sulfur dioxide, sulfur trioxide, and carbon dioxide. Equation (2) applies to salts of these acids also. However, hydrogen chloride is considered to be the major source of salt deposits in crude units. Several of these other acids (ie: sulfide, acetate, bisulfide) form salts which are much more volatile than ammonium chloride (K is large). For example, at 250 °F (121 °C) the equilibrium vapor pressure of ammonium acetate is approximately 30 times greater than ammonium chloride. Ammonium sulfide is much more volatile (about 11 orders of magnitude higher vapor pressure than ammonium chloride). The concentrations of acid and base needed to generate the required partial pressures of these salts are much greater than found in most crude units at typical ammonia or amine feedrates and acid concentrations.

Other acids form salts (ie: bisulfate, sulfate) which are very non-volatile (K is small) but are usually present in concentrations (P_{HA} is small) too small to form appreciable quantities of salt except in isolated instances.⁽³⁾

The total pressure exerted by a volatile salt is given by:

$$P = P_B + P_{HA} \quad (3)$$

Variation of the total pressure as a function of temperature is given by the Clapeyron⁽⁴⁾ equation:

$$d(\ln P) / dT = \Delta H_v / RT^2 \quad (4)$$

where ΔH_v is the enthalpy of vaporization. Assuming that ΔH_v is a constant over the relevant range of temperature and integrating yields:

$$\ln(P_2/P_1) = (-\Delta H_v/R)(1/T_2 - 1/T_1) \quad (5)$$

If P_1 is set to 1 atmosphere, then T_1 is the normal boiling point (T_B). Equation (5) can then be rewritten as:

$$\ln(P_2/1\text{atm}) = -\Delta H_v/RT_2 + \Delta H_v/RT_B \quad (6)$$

The second term is a constant and equation (6) can be simplified to:

$$\ln(P/1\text{atm}) = -\Delta H_v/RT + \text{constant} \quad (7)$$

Thus, a plot of $\ln(P/1 \text{ atm})$ vs. $1/T$ yields a straight line of slope $-\Delta H_v/R$.

An example of an equilibrium vapor pressure plot is shown for ammonium chloride in Figure 1. Historically^(5,6), equilibrium vapor pressure functions for ammonium chloride have been used to predict the potential for ammonium chloride to deposit in crude units. To accomplish this, computer programs were developed which calculate P_B and P_{HA} of ammonia and hydrochloric acid under crude unit operating conditions. For temperatures at which P' (the sum of the actual partial pressures of NH_3 and HCl) is greater than P (the equilibrium vapor pressure of ammonium chloride), solid ammonium chloride will exist. The temperature at which initial precipitation of ammonium chloride occurs is referred to as the salt dewpoint.

Although the vapor pressure function of ammonium chloride is well known and used to predict ammonium chloride dewpoints, vapor pressure functions of amine hydrochlorides have not been reported. In fact, it has been stated in the literature that the volatility of amine salts is a relatively unimportant selection factor.⁽⁷⁾

This paper will demonstrate that the volatility of the neutralizer salt is a very important criterion in neutralizer selection. A new approach toward alleviating salt deposition and corrosion problems is to select neutralizers which form hydrochloride salts of sufficient volatility so that precipitation will not occur above the water dewpoint. This new approach toward neutralizer selection was developed by use of Knudsen effusion to determine equilibrium vapor pressure functions of neutralizer hydrochloride salts as well as ammonium chloride. A spreadsheet was developed to calculate salt dewpoints based on these equilibrium vapor pressure functions and crude unit operating conditions. These salt dewpoint calculations and several field studies have shown that crude units exist which cannot be treated by traditional neutralizers without the potential for salt deposition. To address the needs of these crude units, a research program was conducted which resulted in several new neutralizers which form more volatile hydrochloride salts than traditional neutralizers.⁽⁶⁾ A case history is presented which describes the successful application of this new neutralizer technology to a crude unit where previous neutralizer programs formed salt deposits which contributed to fouling and corrosion.

EXPERIMENTAL

Salt Vapor Pressure Determination

The equilibrium vapor pressure functions of neutralizing amine hydrochloride salts and ammonium chloride were determined by Knudsen effusion. A complete description of the theory of Knudsen effusion and the techniques used to measure vapor pressure are found in Experimental Physical Chemistry.⁽⁹⁾ The basic theory used to determine the vapor pressure of a solid or liquid material by Knudsen effusion is that the rate at which gas molecules in equilibrium with a solid escape through a small orifice into a vacuum is directly proportional to the vapor pressure under certain experimental conditions. In order for this to be a simple relationship, it is necessary that the pressure outside the orifice be sufficiently low so that the mean free path of the molecules (the average distance travelled by a gas molecule between collisions) is long compared with the thickness and diameter of the orifice.

To obtain equilibrium vapor pressure functions of amine salts, the salts are heated to various temperatures, under vacuum, in "Knudsen cells". The vapor pressure at a specific temperature is calculated from the following equation:

$$P = (m/C)(2\pi RT/M)^{1/2} \quad (8)$$

where m is the mass flux from the cell ($\text{g}/\text{cm}^2/\text{s}$), M is molecular weight (g/mole), T is the temperature (K), and R has the units of $\text{ergs}/\text{K}/\text{mole}$; P is obtained in dynes/cm^2 . C is a dimensionless correction factor referred to as a "Clausing Factor". This correction is necessary to account for non-zero thickness of the orifice and the resistance to effusion caused by collisions within the orifice.

Vapor pressure/temperature data are plotted and fitted per equation (7) to allow calculation of the total vapor pressure at temperatures of interest. Figure 2 is an example of the data and fitted equation for Amine E · HCl.

LABORATORY RESULTS

Salt Precipitation Potentials of Traditional Neutralizers

To compare the potentials of neutralizing amine hydrochlorides to precipitate, a Precipitation Potential Index (PPI) was developed. The PPI is determined by dividing the average equilibrium vapor pressure of ammonium chloride over the temperature range of 225 °F (107 °) to 300 °F (149 °C) by that of an amine hydrochloride. Therefore, the lower the equilibrium vapor pressure of an amine salt, the higher its precipitation potential. The PPI's for several traditional neutralizers are shown in Table 1. Of the neutralizer hydrochloride salts evaluated, Amine A had by far the highest precipitation potential, 140 times that of ammonium chloride. All of the other neutralizers (with the exception of Amine E) also had PPI's higher than ammonium chloride.

Development of Low Salt Precipitation Potential Neutralizers

Salt dewpoint calculations (discussed in Field Results section) revealed that in some crude units, none of the traditional neutralizers would be expected to form hydrochloride salts with initial salt dewpoints lower than the water dewpoint. Based on those calculations, it was apparent that a need existed for new neutralizers which form more volatile hydrochloride salts. A research program was initiated to develop new neutralizers which meet this criterion. Numerous materials were initially considered as possible low precipitation potential neutralizers. Various factors were used to determine the most suitable candidates. These factors included salt precipitation potential, water dewpoint neutralization, cost, buffering, toxicity, and environmental acceptability.

From the original list of possible neutralizers, five materials were chosen as suitable for use as low salt precipitation potential neutralizers. The greatly reduced salt precipitation potentials for these new materials are shown relative to ammonia in Table 2.

FIELD RESULTS

Calculation of Salt Dewpoints

A spreadsheet was developed to determine the likelihood of salt deposition under crude unit conditions. The spreadsheet utilizes the concentrations of neutralizing amines (or ammonia) and chloride in the crude unit and operating conditions of the unit to calculate partial pressures of amine (or ammonia) and hydrogen chloride. From these partial pressures, the salt equilibrium quotient is calculated. The spreadsheet utilizes the equilibrium constant function of the salt to determine the temperature at which the vapor would be in equilibrium with the solid salt. This temperature is referred to as the Initial Salt Dewpoint. A list of the information required to calculate Initial Salt Dewpoints is shown in Table 3.

To determine the likelihood of salt deposition in a crude unit, the Initial Salt Dewpoint and water dewpoint are compared. If the Initial Salt Dewpoint is greater than the water dewpoint, then high temperature corrosion and fouling can occur. As the hydrocarbon is cooled to below the Initial Salt Dewpoint, the sum of the partial pressures of the amine (or ammonia) and hydrogen chloride becomes greater than the equilibrium salt vapor pressure and salt precipitation occurs to maintain equilibrium. As further cooling occurs, this precipitation can continue until either the acidic or basic component of the salt is depleted or the water dewpoint is reached.

Field Studies

Study 1. Severe salt deposition occurs above the water dewpoint in the air condensers of a crude unit of this Gulf Coast refinery. Intermittent water washes are used to remove this deposit. The neutralizer product applied at this unit contains equal concentrations of Amine A and Amine C. Salt dewpoint calculations predict that the hydrochloride salt of Amine A has an initial dewpoint of 344 °F (173 °C), well above the water dewpoint of 230 °F (110 °C), Amine C has an initial salt dewpoint of 241 °F (116 °C), only slightly above the water dewpoint.

Analysis of aqueous samples collected from the water boot of the overhead accumulator (Table 4), both before and during a water wash, confirmed the greater potential for salt deposition of Amine A compared to Amine C. Before the start of the water wash (0 minutes), the concentration of Amine A was one third that of Amine C. Based on neutralizer product composition, and oil/water distribution characteristics, equal concentrations of Amine A and Amine C were expected in the water phase. It was evident that two thirds of Amine A fed into this system was not reaching the accumulator. As shown in Table 4, during the water wash tremendous increases in concentrations of Amine A and chloride were measured. This confirmed that much of Amine A had deposited as the hydrochloride salt and was removed by the water wash. Since the concentration of Amine C did not increase during the water wash, it was believed to not have deposited.

To determine which neutralizers could be applied in this system without the potential for salt deposition, additional salt dewpoint calculations were performed for traditional and low salt precipitation potential neutralizers at concentrations of equal neutralizing strength to the current neutralizer product. These results (Figure 3) show that low salt precipitation potential neutralizers (Amines H, I, and J), all have predicted salt dewpoints well below the water dewpoint and are not expected to contribute to salt deposition. Amines A through D have predicted salt dewpoints higher than the water dewpoint and are not recommended for this system. The predicted salt dewpoint of Amine E is approximately equal to the water dewpoint making this neutralizer a marginal choice for this system.

Study 2. This midwestern asphalt unit has experienced high corrosion rates (up to 50 mpy) in an overhead exchanger at 350 °F (177 °C) to 375 °F (207 °C), well above the water dewpoint of 230 °F (110 °C). A product containing predominantly Amine B is fed to the unit prior to the inlet of the problem exchanger. Since the initial salt dewpoint of Amine B was predicted to be 420 °F (216 °C), salt deposition is considered to be the source of this corrosion. This product was discontinued and another neutralizer product was fed which did not contain Amine B. Evidence of salt deposition due to Amine B was provided by analysis of water samples collected from the accumulator for two weeks after Amine B was discontinued. The results of these analyses are shown in Figure 4. The results show that Amine B persisted in the system for at least two weeks after its feed was discontinued. This is

believed to be due to the sublimation of existing Amine B salt deposits which occurred as the partial pressure of Amine B in the system gradually decreased.

Study 3. Neutralizer hydrochloride salt deposits have caused corrosion and fouling on overhead exchangers above the water dewpoint in a crude unit of this midwestern refinery. The neutralizer product applied at this refinery contains a 4:1 weight ratio of Amine B to Amine C, both of which form low melting point, hygroscopic salts which are liquid at overhead temperatures. Deposits on overhead bundles were dissolved and samples collected during a steamout prior to removing the bundles for inspection. Analysis of the steam condensates showed a 31:1 ratio of Amine B to Amine C. Sufficient chloride was present in these samples to indicate that both neutralizers were present as the hydrochloride salts. The ratio of Amine B to Amine C was much greater in the steam condensates than the neutralizer product fed to this system. These results show that amine B has a greater tendency to deposit in this system than Amine C. These results correlate qualitatively with experimentally determined salt precipitation potentials (Table 1) which show that amine B has a higher salt precipitation potential than Amine C.

Initial Field Trial of Low Salt Precipitation Potential Neutralizers

The initial field trial of a low salt precipitation potential neutralizer product (Amine J) was conducted at an Oklahoma refinery. The purpose of this initial trial was to determine the ability of the new neutralizer to elevate pH at the water dewpoint relative to the overhead accumulator and provide information to aid in formulating additional low precipitation potential neutralizer products.

The new neutralizer proved to be successful at elevating both accumulator and water dewpoint pH values. The pH at the water dewpoint was monitored by water samples obtained with a COLA (Condensate On Line Analyzer). This monitoring device provides controlled condensation of overhead vapors and determination of the water dewpoint temperature. The pH at the accumulator was elevated to 5.6 with neutralizer compared to 4.5 when no neutralizer was fed. Dewpoint pH values were 6.0 and 4.8, respectively.

Case History

A Northwestern crude unit (see Figure 5) overhead treated with a traditional neutralizing amine blend experienced general corrosion rates of 15 to 20 mpy and pitting rates of about 350 mpy. Those rates were measured on probes and/or coupons exposed at about 250 °F (121 °C) between the first and second exchangers in the overhead of the second column. This unit processes a blend of Alaskan North Slope and Peace River crudes. The second tower overhead temperature is about 300 °F (149 °C). High accumulator iron concentrations and several tube leaks during the first half of 1993 confirmed the fact that corrosion performance was unacceptable.

The traditional neutralizer (a blend of amines D and E) exhibits excellent salt properties.^(10, 11) The hydrochloride salts of both D and E are low melting point, hygroscopic, and exhibit good dispersability in a hydrocarbon matrix. Despite these attributes, salt fouling was suspected based on the appearance of coupons pulled from the system after 15 days of exposure (see Figure 6 at bottom). The coupons were cleaned by glass beading to allow examination of the metal surface. The fact that severe under deposit corrosion was occurring is shown in Figure 7 at bottom.

A portion of the deposit from that coupon was extracted with water and analyzed by gas chromatography with a nitrogen specific detector. The extract contained about 1800 ppm amine D and about 70 ppm amine E. These results are consistent with the relative salt volatilities of amine D and E as shown in Table 1.

Based on the analytical evidence of salt fouling and corrosion, a product based on amine F was recommended. This amine forms a hydrochloride salt which is two to eight times more volatile than those of amine E and D, respectively. Within several days of the product change, accumulator iron concentrations decreased from about 10 ppm to 3 ppm. The first coupon pulled after about three weeks showed 3 mpy. Photographs of the second coupon pulled after 14 days (compared to one from the traditional amine program) are shown in Figures 6 and 7. The great reduction in deposition and localized corrosion is obvious.

The second coupon (which was exposed for a shorter time than the first) showed a higher corrosion rate of 6 mpy. Water extracts of the entire deposit from that coupon contained about 50 ppm of amine F. Somewhat surprisingly, a higher concentration (about 85 ppm) of amine D was detected in the extract even though it had not been fed to the system for over two months. This is taken as evidence of a slow sublimation or sloughage of previously laid down salts from the overhead line and first exchanger.

CONCLUSIONS

1. Based on measured equilibrium vapor pressures and the partial pressures of acids in most crude overheads, the salts of hydrogen chloride are the most likely ones to cause fouling and corrosion problems above the dewpoint of water.
2. Analyses of intermittent water wash and "steamout" samples confirm the occurrence of amine hydrochloride salt deposition. The persistence of traditional amines in accumulator waters after product changes have been made also indicated that deposits exist in overhead equipment.
3. Traditional approaches to neutralizer selection (salt melting point, hygroscopicity, etc.) have not always been successful because salt volatility, the thermodynamic driving force for salt formation, has not been considered. Hydrochloride salts of traditionally used amines exhibit a volatility range of about 200-fold at between 225 °F (107 °C) and 300 °F (149 °C).
4. New neutralizers have been developed which form hydrochloride salts as much as 50 times more volatile than the best traditional amines. These new products have alleviated fouling and corrosion problems in several overhead systems.
5. Salt dewpoint calculations have shown utility in predicting the occurrence of deposition in overhead systems and in selecting traditional or novel approaches to overhead neutralization.

ACKNOWLEDGEMENTS

Contributors to the laboratory data presented in this paper were W. J. Delaney, C. R. Frey, C. Garcia, and R. E. Tupper. Without their diligent efforts, this paper would not have been possible.

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TABLE 1
RELATIVE PRECIPITATION POTENTIALS FOR HYDROCHLORIDE SALTS
OF TRADITIONAL NEUTRALIZING AMINES
 NO H₂S IN TEST SOLUTIONS

Neutralizing Amine	Salt Precipitation Potential Index
A ETHYLENE DIAMINE	140
B METHYL ETHYL AMINE	6.4
C AMOPA	2.6
D DIMETHOXYETHANOL AMINE	2.1
Ammonia	1.0
E DIMETHYL ISOPROPYL AMINE	0.58

TABLE 2
RELATIVE PRECIPITATION POTENTIALS FOR HYDROCHLORIDE SALTS OF
NOVEL NEUTRALIZING AMINES
 OIL SOLUBLE

Neutralizing Amine	Salt Precipitation Potential Index
Ammonia	1.0
F	0.26
G	0.18
H	0.10
I	0.10
J	0.01

TABLE 3
INFORMATION REQUIRED FOR SALT DEWPOINT CALCULATIONS

Crude Charge Rate
Water-in-Crude
Stripping Steam Rate
Total Overhead Flow
Overhead Temperature
Overhead Pressure
Accumulator Temperature
Accumulator Pressure
API Gravity of Overhead Naphtha
Distillation Curve of Overhead Naphtha
Chloride Concentration
Neutralizer Feedrate
Equilibrium Vapor Pressure
Curve of Neutralizer
Hydrochloride Salt

TABLE 4
GULF COAST REFINERY
INTERMITTENT WATER WASH STUDY ACCUMULATOR WATER ANALYSIS

<u>Analyte, ppm</u>	<u>TIME FROM START OF WATER WASH, MINUTES</u>								
	<u>0</u>	<u>5</u>	<u>10</u>	<u>15</u>	<u>30</u>	<u>50</u>	<u>90</u>	<u>150</u>	<u>210</u>
Cl	34	4160	2820	1810	670	246	115	74	75
Amine A	21	3700	2500	1700	550	140	52	22	21
Amine C	69	51	51	41	25	22	23	29	33
Fe	0.1	34	59	26	2.3	2.2	1.4	0.6	0.4
NH ₃	141	156	163	166	155	88	57	80	84
Acetic Acid	18	23	24	19	19	20	22	27	21
Butyric Acid	5	6	6	4	5	5	6	6	6
Propionic	8	6	7	7	7	8	8	9	8
C ₅ to C ₇ Acids	70	36	36	28	44	61	67	73	73

TYPICAL REFINERY APPLICATIONS

CORROSION INHIBITORS

ANTIFOULANTS

UOP REFINING CHEMICALS

UNICOR PROCESS CORROSION INHIBITORS

Unicor 30% Active Weight

Unicor M 60% Active Weight

Oil Soluble Amine Salt

Naphtha Solvent

Unicor and Unicor M are of medium to low dispersency and are used in distillation towers within a 4.5 to 8.0 pH range. These are a good all around inhibitors but is usually used in areas where C_5 + hydrocarbons are present for solvency. A typical Unicor dosage of 6-12 ppm and Unicor M dosage of 3-6 ppm by weight are used. Unicor M has been used for military jet fuel (NACE test) at 4 lb./M bbl. It is effective for both corrosion inhibitor and rust inhibitor properties.

Unicor A 34% Active Weight

Oil Soluble Amine Salt

Oil Soluble Amine Polymer Dispersant

Naphtha Solvent

Unicor A is a moderately high dispersant version of Unicor. The corrosion inhibitor and dispersant are oil soluble. Effective pH range is 4 to 9. Typical dosages are from 4 to 8 ppm by weight.

Unicor C 20% Active Weight

High Molecular Weight - Oil Soluble

Petroleum Solvent

Unicor C has very low detergency and has good light hydrocarbon solvency. It is used in crude units where WSIM characteristics, such as for jet fuel, are important. Due to its low detergency, it is best used in areas of 5 to 7.5 pH range. Typical dosage is 2-8 ppm by weight.

ANTIFOULANT ADDITIVES FOR REFINING PROCESSES

Unicor LHS: 50% Active Weight

Amine Salt of Organic Acid Phosphate
Petroleum Solvent

Unicor LHS has been used as a detergent to remove inorganic deposits from light ends towers. On stream cleaning dosage is 15 to 50 ppmw. Unicor LHS is an effective antifoulant to prevent deposits in refinery compressors. A typical dosage is one pint per million cubic feet of compressor feed. Unicor LHS does not require solvent dilution.

Polyflo 100: 50% Active Weight

High Molecular Weight Amine Polymer
Aromatic Hydrocarbon Solvent

Polyflo 100 is used as an antioxidant dispersant stabilizer and anti-foulant for heavier hydrocarbons. Typical antifoulant additive dosage has range rom 15 to 50 ppm. Dosage of 100 ppm has been used to clean residual and reclaimed lube oil tankage. Polyflo 100 has been tested in crude unit feed train at up to 800°F, as an antifoulant.

Polyflo 140: 50% Active Weight

Polyamino Polyol
Hydrocarbon Solvent

An antifoulant designed to be effective where winter time handling properties are of concern. Used as an antifoulant for gas oil feed to an FCC unit at 18 ppmw. The antioxidant and dispersant properties fall between Polyflo 100 and Polyflo 130.

Polyflo 130: 50% Active Weight

Polyamino Polyol
Aromatic Hydrocarbon Solvent

Polyflo 130 is widely used as a dispersant stabilizer in finished diesel fuel and as a multifunctional antifoulant in naphtha to gas oil process feed streams. A typical dosage, depending on fouling severity, is 12 to 15 ppm by weight. It has proven effective in a crude exchanger stream at 12 to 18 ppm by weight. Polyflo 130 had been tested and approved by a major oil company for use in streams up to 800°F. It is recommended for use where the fouling is primarily of organic origin.

CRUDE TOWER OVERHEAD:

Neutralizer: UOP strongly recommends that ammonia be used as the neutralizer of choice. It is, by far, much less expensive than the commercial neutralizing amines on the market. Ammonia's main advantage is that the ammonium salts, such as ammonium chloride and ammonium hydrosulfide, are very watersoluble. As hydrocarbon chains are added to ammonia to make the organic amine neutralizers, the solubility of the amine and the amine salts become much less watersoluble and the material formed by neutralization becomes more oil soluble. The oil soluble material now becomes a problem with operation of downstream catalytic units.

The disadvantage of anhydrous ammonia is that it is not only a neutralizer but a refrigerant. As pressure is reduced, the ammonia condenses and then, as heat is added, again becomes a gas. If this is properly considered in the design of neutralizing injection equipment, pH is relatively easy to control. Neutralizing amines, being a dilute product, are easy to add with additive pumps. However, neutralizing amines added at equal mole ratios as ammonia, cost 35 to 55 times more than ammonia. On a 5,000 b/d crude unit, the savings with the use of ammonia will pay for an automated pH control system in less than one year.

Corrosion Inhibitor: Our inhibitor of choice for most crude unit overhead applications is Unicor M. This concentrated oil soluble inhibitor is used at 3-6 wt-ppm. Injection rate varies with concentration of corrosion species and pH control. A typical dosage is 4 wt-ppm for most applications. The use of an oil soluble inhibitor is recommended where automatic pH controllers are used.

Vacuum Tower Overhead: Corrosion in a vacuum tower overhead is usually due to oxygen ingress into the system. The best corrosion control is to seal against leakage into the tower overhead system.

Coker:

Fouling of coker tubes can be a problem. As this is a high temperature operation, we believe that polysiloxane (silicone) is the additive of choice. However, at the 120 ppm minimum of silicone needed to protect against carbon buildup, the breakdown of silicone can be a severe catalyst contaminant in coker overhead products processed in downstream units. We recommend that an additive not be used.

Alkylation (H_2SO_4) Unit:

In sulfuric acid unit, the sulfuric acid esters formed will exit with the product. The most effective corrosion protection is the hot water wash. The sulfuric acid esters are only water soluble in hot water. The water wash product enters the deisobutanizer where unwashed esters are boiled overhead. Corrosion inhibitors such as Unicor LHS at 2 wt-ppm or Unicor C at 3 wt-ppm have been used to protect the tower, however the deisobutanizer overhead recycles back to the feed where the amine inhibitor is decomposed by the H_2SO_4 and the products formed contribute to the sulfuric acid ester problem.

Sulfolane/Aromatics Separation:

Oxygen entering the system via the hydrocarbon or solvent can result in corrosion in the towers. A corrosion inhibitor will arrest the corrosion, however, we do not recommend that inhibitor be used in these systems. Corrosion inhibitors can effect the surface tension and solubility of the aromatics in the solvent. As the corrosion inhibitor accumulates in the system, the product yields decline. The addition of UOP SX solvent antioxidant to the solvent will inhibit the formation of polymeric acids, reducing corrosion.

Distillate Desulfurizer:

If fouling is due to organic polymerization and gums, an antifoulant can be very effective. If an additive, such as Polyflo 130 or Polyflo 140 can be added upstream prior to peroxide formation leading to sediment formation, as little as 12 to 15 wt-ppm of the antifoulant will provide protection. If additives are applied just ahead of the unit feed exchangers, 20 to 25 wt-ppm of antifoulant may be necessary to inhibit and disperse the foulant.

The stripper tower after the reactors may experience corrosion if chlorides are present. Reformer hydrogen may contain chloride salts which will end up in the tower overhead. Unisor LHS or Unisor C used at 2-3 wt-ppm will be effective.

Hydrocracker:

Where organic fouling in the feed exchangers is a problem, Polyflo antifoulants can be used to keep asphaltines and waxes dispersed. Dosage of antifoulant can be adjusted based on the rate of fouling. As metals such as Nickel and Vanadium are known catalysts to promote fouling, and these metals are usually present in Hydrocracker feed streams, a relative high dosage of antifoulant is usually required. Polyflo 130 or Polyflo 100 used a 25 wt-ppm may be required to control sediment formation and to disperse asphaltines.

The debutanizer overhead exchangers are usually exposed to high levels of ammonium sulfide due to high nitrogen and sulfur levels in hydrocracker feed. Unisor LHS at 4 wt-ppm is recommended to inhibit against corrosion and help prevent deposition of ammonium sulfide in the debutanizer overhead exchangers.

Recycle gas compressors can experience problems of fouling due to entrained contaminants in the gas stream. Unico LHS at 1 pint per million cubic feet of gas can be injected in the compressor feed to enhance onstream efficiency of the exchangers.

CORROSION INHIBITOR APPLICATIONS

<u>UNIT</u>	<u>DOSAGE BY ACTIVE WEIGHT</u>	<u>INHIBITOR TYPE</u>
CRUDE TOWER OVERHEAD	2 to 4 ppm 2 to 4 ppm	AMINE SALT IMIDAZOLINE
ALKYLATION UNIT (Sulfuric) DEPROPANIZER TOWER	1 ppm 2 ppm	AMINE PHOSPHATE ESTER AMINE
FLUID CATALYTIC CRACKER MAIN FRACTIONATOR TOWER	1 to 3 ppm	AMINE SALT IMIDAZOLINE
LIGHT END TOWER OVERHEAD	1 to 5 ppm	AMINE PHOSPHATE ESTER
NAPHTHA DESULFURIZER HYDROCARBON FEED	8 to 10 ppm	ANTIFOULANT POLYAMINE POLYOL
STRIPPER TOWER OVERHEAD	0.5 to 1 ppm	AMINE PHOSPHATE ESTER AMINE
REFORMER STABILIZER (Stripper) OVERHEAD	1 ppm 2 ppm	AMINE PHOSPHATE ESTER AMINE
DISTILLATE DESULFURIZER HYDROCARBON FEED (Before Tankage)	6 to 8 ppm 6 to 20 ppm	POLYAMINE POLYOL AMINE STABILIZER PLUS DISPERSANT
HYDROCARBON FEED (Before Exchangers)	10 to 12 ppm 10-25 ppm	POLYAMINE POLYOL AMINE STABILIZER PLUS AMINE SULFONATE DISPERSANT
HYDROCRACKER HYDROCARBON FEED COMPRESSOR FEED	12 to 25 ppm 5 ppm	<u>ANTIFOULANT</u> POLYAMINE AMINE PHOSPHATE ESTER
DEBUTANIZER OVERHEAD	2 ppm	AMINE PHOSPHATE ESTER
POLYMERIZATION UNIT STABILIZER OVERHEAD	0.5 to 2 ppm	AMINE PHOSPHATE ESTER

d. Special Application

1) Ammonia Addition to Crude Tower Feed

Some refiners have approached the overhead system corrosion problem from a very different point of view: by neutralizing the HCl before it gets to the overhead system or even before it evolves. Caustic is added to the desalted crude (feed to the crude column) to react with the unstable calcium and magnesium chlorides and convert them to the more stable sodium chloride salt which does not hydrolyze and is stable at maximum crude feed temperatures.

Ammonia as ammonium carbonate or ammonium hydroxide is injected downstream of the caustic injection point. The caustic reacts with naphthenic acids in the desalted crude, and as chlorides are hydrolyzed at the 300° to 450°F temperatures, sodium chloride is formed. The ammonia is said to aid the reaction, and appears to result in a complete reaction where very little HCl is formed in the crude overhead accumulator water. Chlorides can be controlled within the 10 ppm chloride target. The technique must be carefully controlled and it must be remembered that if either the caustic or ammonia pump stops, the reaction stops, allowing unreacted chlorides to go into the overhead. The treatment does not suggest the use of corrosion inhibitors, but very careful control is required and allowance should be made for injection equipment failure.

2) Advantages of Injecting Ammonia to the Feed

By eliminating the formation of hydrogen chloride, the corrosion in the overhead has been controlled. Condensation of water is not as critical as it is when large quantities of hydrogen chloride are present. Alloy materials are no longer

necessary for the overhead system. Nevertheless, some localized corrosion has been experienced.

Ammonium chloride, which results from an ammonia-inhibitor system, is no longer present. Ammonium chloride has caused fouling of the overhead condensers and has been carried over into naphtha desulfurization units causing fouling and corrosion.

Crudes with salt contents as high as 40 PTB can be effectively controlled. Conventional overhead neutralization systems are limited to feed salt contents less than 20 PTB to avoid excessive fouling and plugging from ammonium chloride in the overhead and salts in the crude preheat train. Experiences have shown a reduction in preheat exchanger fouling with the feed additive system since the sodium naphthenates formed in the reaction are natural detergents and perform as anti-foulants.

3) Limitations of Injecting Ammonia to the Feed

Should there be a sudden production of HCl in the tower, the presence of ammonia will cause its neutralization. When ammonium chloride levels increase, the higher partial pressure of ammonium chloride results in its desublimation in the crude tower. The salt is then withdrawn as part of the side cuts and can result in corrosion in new areas. The salt deposits remaining in the tower will cause poor performance and can result in localized under-deposit corrosion. For complete protection of double drum systems, the temperature of the cooling fluid must be above the water dew point of the overhead vapor. Otherwise, localized water condensation/vaporization can create a corrosive condition with less than 10 ppm chlorides in the total condensed water.

The technique of adding caustic and ammonia compounds in the feed is effective as long as all pumps are operating. When both pumps stop, the system is completely unprotected. If only one

pump stops, care in control must be exercised to keep pH and chlorides within a safe operating range. Corrosion inhibitor injection into the overhead system on a continuous basis at a minimum level will allow for minor upsets and the dosage can then be raised during major control problems.

PROBLEM:

Determine the ammonia flow rate needed to neutralize 50 ppm chlorides present in the tower overhead receiver water.

DATA:

Feed to tower: 150,000 BPSD
Overhead product (Naphtha) 30 vol % of feed
Water in overhead system: 5 vol % based on overhead product
Gravity of overhead product 55° API (265 lb/Bbl)
Tower overhead pressure 20 psig
Aqueous Ammonia available at 30 vol %

CALCULATIONS:

$$\text{Naphtha Flow} = \frac{(150000 \text{ Bbl})}{\text{Day}} (0.30) = 45000 \text{ Bbl/day}$$

$$\begin{aligned} \text{Water Flow} &= (45000 \frac{\text{Bbl}}{\text{Day}}) (0.05) \frac{(42 \text{ gal})}{\text{Bbl}} \frac{(8.33 \text{ lb})}{1 \text{ gal}} \\ &= 787185 \text{ lbs/day} \end{aligned}$$

$$\begin{aligned} \text{Chlorides as HCl} &= (787185 \text{ lb of water/day}) \frac{(50 \text{ lb HCl})}{10^6 \text{ lbs water}} \\ &= 39.4 \text{ lb HCl/day} \end{aligned}$$

Since $\text{NH}_3 + \text{HCl} \longrightarrow \text{NH}_4\text{Cl}$ and for each mol of HCl (35.5 lb) it is required one mole of NH_3 (17 lb),

$$\begin{aligned} \text{Then flow of ammonia needed} &= 39.4 \frac{\text{lb HCl}}{\text{day}} \frac{(17 \text{ lb NH}_3)}{35.5 \text{ lb HCl}} \\ &= 18.8 \text{ lbs/day} \end{aligned}$$

With a 30% solution, the flow should be:

$$\begin{aligned} \text{flow 30\% solution ammonia} &= 18.8 \frac{\text{lb NH}_3}{\text{day}} \frac{(1 \text{ lb solution})}{0.30 \text{ lb ammonia}} \\ &= 62.8 \text{ lbs/day} \\ &= 3.76 \text{ cubic foot/day} \end{aligned}$$

PROBLEM:

Determine whether anhydrous ammonia can be used for the previous system.

Additional Data:

Ambient Temperature	60°F
Ambient conditions	No wind
Ammonia cylinder area	12.5 ft ²
Heat transfer to cylinder	1.7 BTU/hr - °F - ft ²

CALCULATIONS:

NH₃ rate: 0.78 lb/hr for 50 ppm Cl⁻ system (as calculated previously). Any ammonia injection system must be able to handle a 100 ppm chlorides in tail water situation. Therefore, for design purposes, rate of ammonia will be set at 1.6 lb/hr.

From Fourier equation,

$$\begin{aligned}\Delta T &= Q/AU = \frac{mH}{AU} \\ &= \frac{(1.6 \text{ lb/hr})(518.1 \text{ BTU/lb})}{(12.5 \text{ ft}^2)(1.7 \text{ BTU/hr} - ^\circ\text{F} - \text{ft}^2)} \\ &= 39^\circ\text{F}\end{aligned}$$

Where 518.1 BTU/lb is the latent heat of vaporization for ammonia at 60°F (Table 6)

$$\text{Steady state temperature} = 60^\circ\text{F} - 39^\circ = 21^\circ\text{F}$$

For T = 21°F, the vapor pressure of ammonia is 49.4 psia.

Since the vapor pressure of ammonia (49.4 psia) is higher than the column overhead pressure (35 psia) the system will work for such conditions described above. Anhydrous ammonia can be used.

THE AUTHOR

Trevor Kletz retired from the chemical industry in 1982 after 38 years service; for the last 14 he was safety adviser to ICI Petrochemicals Division and was particularly concerned with process safety and loss prevention. He is now a part-time member of the staff of the Department of Chemical Engineering at Loughborough University of Technology.

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ISBN 0-85295-167-1 2nd edition 1985

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