## CHAPTER SEVEN

# **Treating Processes**

Thioalcohols or thiols, more commonoly known as *mercaptans*, are a family of organic sulfur compounds present in a wide variety of untreated petroleum distillates, such as LPG, naphtha, kerosene, and gas oils. Specific mercaptans found in petroleum distillates originate in the crude or may form during subsequent crude refining. The concentration of these mercaptans in the crude distillate depends on the origin and sulfur distribution in the crude.

Mercaptans are undesirable in petroleum products. In the lower boiling range, they are moderately acidic and characterized by an extremely offensive odor. These properties diminish as mercaptan molecular weight increases. Thiophenol, which is an aryl mercaptan and more acidic than alkyl mercaptan, is found principally in cracked hydrocarbons. Thiophenol is undesirable in finished gasoline because it produces an unstable gasoline by promoting hydroperoxidation of olefins to gum. In summary, mercaptans are undesirable in finished petroleum products as they adversely affect the product's odor, stability, and quality, apart from being corrosive to the refining and handling equipment.

### **GENERAL PRINCIPLES**

In the early days of refining industry, mercaptan removal was done with the classic "Doctor solution." The Doctor treatment<sup>1</sup> consists of contacting the oil with a little sulfur and alkaline sodium plumbite solution, as follows:

 $2 \text{ RSH} + \text{Na}_2\text{PbO}_2 = (\text{RS})_2\text{Pb} + 2 \text{ NaOH}$ 

 $(RS)_2Pb + S = R_2S_2 + PbS$ 

Lead sulfide is reconverted to plumbite by heating the alkaline solution to 150–175°F and blowing with air, which converts sulfide to plumbite.

Lead sulfide itself was also used as sweetening agent.<sup>2</sup> The overall reaction is same as that given by the Doctor solution. The process consists in contacting sour distillate stream with sodium sulfide and lead sulfide suspended in caustic solution and air.

These treating processes are associated with high process losses in the form of leaded sludge. Also, water used in washing operations contain lead sulfide, which makes them no longer acceptable for any use and presents a disposal problem due to environmental concerns.

The UOP Merox process is a catalytic chemical treatment for petroleum distillates to remove mercaptants or convert them to disulfides. The process is based on the ability of catalysts composed of iron group metal chelates to promote the oxidation of mercaptans to disulfides using air as the source of oxygen. The overall reaction is as follows:

 $4RSH + O_2 = 2RSSR + 2H_2O$ 

In this equation, R represents a hydrocarbon radical, which may be aliphatic, aromatic, or cyclic, saturated or unsaturated. The reaction is carried out in an alkaline medium, in the presence of a Merox catalyst at  $90-120^{\circ}$ F.

# FCCU LIGHT GASOLINE

Light gasoline from the FCCU may contain 130 ppm or more mercaptan sulfur, which must be reduced to 5 ppm before this stock can be considered suitable for blending in gasoline grades (see Figure 7-1).

FCCU light gasoline is brought directly into the Merox reactor from the bottom of the FCCU debutanizer column on flow control reset by debutanizer level control. Tables 7-1 and 7-2 show the unit's feed and product properties.

A  $2-5^{\circ}$  Be (1-3 wt% NaOH) caustic from the caustic storage tank is sprayed into gasoline through an atomizing nozzle. The hydrocarbon/ caustic mixture next enters air mixer MX-101, where a metered amount of air is injected from air compressor C-101 continuously into the gasoline by diffusion through a sintered steel cylinder. The effluent from the air mixer then flows into Merox reactor V-102. The feed is distributed



Figure 7-1. Light gasoline Merox treating.

PROPERTY	UNITS	FEED	PRODUCT
API GRAVITY		69	69
DISTILLATION ASTM			
IBP	°F	105	105
FBP	°F	280	280
H <sub>2</sub> S CONTENT	WT. ppm, MAX	5	0
MERCAPTAN SULFUR	WT. ppm, MAX	130	5
TOTAL SULFUR	Wt%	0.04	0.04
CORROSION, Cu STRIP @ 50°C			MAX NO. 1
PEROXIDE NUMBER*			< 0.3
EXISTENT GUM	mg/100 ml, max		<2
POTENTIAL GUM	mg/100 ml, max		<6
ENTRAINED Na OH	max, ppm		1

# Table 7-1 Feed and Product Properties, FCCU Light Gasoline Merox

\* UOP TEST METHOD 33.

#### Table 7-2

### Feed and Product Properties, FCCU Heavy Gasoline Merox

FEED	UNITS	FEED	PRODUCT
API GRAVITY		33.7	33.7
DISTILLATION ASTM			
IBP	°F	265	105
50%	°F	325	325
90%	°F	380	380
H <sub>2</sub> S CONTENT	WT. ppm, MAX	5	0
MERCAPTAN SULFUR	WT. ppm, MAX	450	5
TOTAL SULFUR	Wt%	0.187	0.187
CORROSION, Cu STRIP @ 50°C			Max No. 1
PEROXIDE NUMBER*			<0.3
EXISTENT GUM	mg/100 ml, max		<2
POTENTIAL GUM	mg/100 ml, max		<6
ENTRAINED Na OH	ppm, max		1

\* UOP TEST METHOD 33.

uniformly across the reactor by a distributor assembly. The reactor is a packed column of activated charcoal over which Merox catalyst has been deposited.

The sweetening reaction takes place in the reactor as the gasoline feed, caustic, and air flow downward through the catalyst bed. The reactor is

operated at approximately 130 psig and 105°F to keep all air dissolved in the gasoline. Any undissolved air can be manually vented to atmosphere from the top of the reactor.

The treated gasoline exits from the reactor through a fine screen located near the bottom of the reactor. The gasoline from the reactor next passes through air eliminator drum V-103, where dissolved air in the gasoline is allowed to disengage at a reduced pressure. Air/hydrocarbon vapor is burned off by mixing with fuel gas. Gasoline is sent to storage after injection of an inhibitor.

The small amount of caustic solution injected into the feed as well as water formed during the reaction are coalesced by the reactor charcoal bed and drop by gravity to the bottom of the reactor. They pass through the drain screen assembly and are sent to disposal under level control.

Impregnation of granular charcoal with Merox catalyst is done in auxiliary equipment. This includes a circulating pump for circulating ammonia water (which is the catalyst carrier), a small drum V-105 for mixing catalyst, an eductor to draw catalyst into ammonia water, and necessary piping to circulate ammonia water. For subsequent catalyst reactivation, a continuous water heater is provided to heat water for washing the catalyst bed of foreign materials adsorbed by charcoal.

## JET FUEL (ATK) SWEETENING

The feed to the unit is, preferably, taken direct from the crude distillation unit with no intermediate storage (see Figure 7-2). Storage of raw kerosene results in unnecessary preaging of naphthenic acids and ingress of oxygen before prewashing. Foaming and color loss problems are enhanced. Raw kerosene feed is heated to 130°F by low-pressure steam in kerosene feed heater H-101. Charge pump P-101 discharges the heated feed to caustic prewash vessel V-102.

In this vessel, the feed is prewashed with a 1.5-2% solution of caustic soda to neutralize both the H<sub>2</sub>S and naphthenic acids present in the feed. Also, to achieve sufficient contact between the caustic soda and the kerosene, the caustic is recycled by recirculating the caustic exiting the prewash vessel and mixing it with the main incoming kerosene stream via charge pump P-101.

The effluent from prewash vessel V-102 should contain no more than 0.005 mg KOH/g as the sum of acidity and sum of equivalent sodium



Figure 7-2. Aviation turbine kerosene (ATK) Merox treatment.

naphthenate present. If naphthenes still exist in the final product, thermal stability and WSIM test values can be adversely affected.

Air is mixed with prewashed kerosene feedstock before entering Merox reactor V-103. The plant air (70 psig) passes through a filter to remove any scale or dirt that would otherwise block the distributor nozzle in the reactor. From the filter, the air passes through a regulator to reduce the pressure to about 60 psig. The air flow, controlled and metered, is next mixed with prewashed kerosene feed through mixer MX-101, which diffuses air into kerosene stream.

The reactor is a packed column of activated charcoal over which Merox catalyst has been deposited. The reactor bed, kept alkaline by periodic circulation of caustic without interruption of the unit feed, also washes off accumulated contaminants. The sweetening reaction takes place in the reactor as the feed, caustic, and air flow downward through the catalyst bed. The reactor is operated at sufficient pressure to keep all air dissolved in the gasoline. Any undissolved air can be manually vented to atmosphere from the top of the reactor.

The treated kerosene exits the reactor through a fine screen located near the bottom of the reactor. The process control consists of checking product mercaptan level, minimizing air injection, and maintaining catalyst alkalinity.

Merox reactor effluent next flows into caustic soda settler V-104, in which any entrained caustic is settled and drained out. The operating pressure of the settler is in the range of 35-40 psig. Tables 7-3 and 7-4 show the jet fuel Merox operating conditions and feed and product properties.

The effluent from the caustic settler next passes through air eliminator drum V-105, where dissolved air in the kerosene is allowed to disengage at a reduced pressure. The vapors from the air eliminator are burned off after mixing with fuel gas.

The air-free product is mixed with washwater and pumped to washwater vessel V-107 to wash out any trace of caustic soda. The quantity of washwater used is approximately 10% of the feed to the vessel. The water used is of boiler feed water quality, free from contaminants. The caustic water that settles down in V-107 is sent to refinery foul water stripper.

The water-washed kerosene is next, it flows to salt filter V-108, where the kerosene is passed through a course bed (3-6 mesh) rock salt for final water elimination.

The final step in the finishing of jet fuel is clay filtration, wherein dried jet fuel is passed through a bed of activated clay in V-109 containing

Table 7-3					
JET FUEL	Merox	Operating	Conditions		

OPERATING PARAMETER	UNITS	RANGE
CAUSTIC PREWASH VESSEL		
TEMPERATURE	°F	125-130
PRESSURE	psig	40-43
CONCENTRATION OF CAUSTIC	VOL/VOL	1.5-2.0%
CAUSTIC CIRCULATION RATIO		
CAUSTIC SODA/KEROSENE	VOL/VOL	5-15%
AIR MIXING SECTION		
AIR/KEROSENE FEED RATIO		
ft <sup>3</sup> PER min AIR/1000 bbl KEROSENE	VOL/VOL	1.1–1.3
REACTOR	0 <b>F</b>	100, 105
	°F	120-125
INLET PRESSURE	psig main	40-42
CAUSTIC CONCENTRATION	psig	2-7
FOR REACTION	Wt%	10
IHSV	$hr^{-1}$	25
CAUSTIC SODA SETTI ED		2.2
PRESSURE	nsig	25-30
TEMPERATURE	°F	120-125
WASHWATER SETTLER	•	120 123
TEMPERATURE	٩°	105
PRESSURE	psig	25-30
SAND FILTER	1 8	
TEMPERATURE	°F	105
PRESSURE INLET	psig	60
PRESSURE OUTLET	psig	58
CLAY TREATER		
(ATTAPULGUS CLAY, 30-60 MESH		
PARTICLE SIZE)		
BULK DENSITY	kg/m <sup>3</sup>	685
SURFACE AREA	m²/gm	95-103
OPERATING TEMPERATURE	°F	110
OPERATING PRESSURE	psi	60-70
SPACE VELOCITY, LHSV	hr"'	1.74
SALT DRIER		
(CRYSTALLINE ROCK SALT)		
2 MESH		DACC TUDOUCU
J MESH		PASS INKOUGH
U MLOH BI II K DENSITV	ka/m <sup>3</sup>	1050 1250
PARTICI E DENSITY	am/cm <sup>3</sup>	1050-1250
SPACE VELOCITY LHSV	$hr^{-1}$	1 00
STICE ( DECCIT, DIG)	***	1.00

	UNITS	KEROSENE FEED	PREWASHED KEROSENE	PRODUCT AFTER MEROX TREATING	SPECIFICATIONS
DISTILLATION, ASTM	- <u> </u>	· · · ·			
IBP		320	320	320	
10%	°F	352	352	352	
20%	°F	356	356	356	
50%	°F	378	378	378	
90%	°F	432	432	432	
FBP	°F	468	468	468	
RESIDUE	vol%	1.0	1.0	1.0	
DENSITY	kg/m <sup>3</sup>	0.790	0.790	0.790	
FLASH POINT	°Č	48	48	48	
FREEZE POINT	°C	-65	-65	-65	
SMOKE POINT	mm	28	28	28	
VISCOSITY –20°C	cst	4.2	4.2	4.2	
WATER SEPARATION					
INDEX MODIFIED WSIM				75	MIN 85
COLOR	SAYBOLT	+30	+26	+24	MIN 21
SULFUR TOTAL	Wt%	0.17	0.17	0.17	
SULFUR MERCAPTANS	ppm	130	130	5-20	20 MAX.
ASTM TOTAL ACIDITY	mg KOH/g	0.01	0.0015	0.0007	0.015 MAX

Table 7-4					
Jet Fuel	Merox	Feed	and	Product	Properties

IBP = INITIAL BOILING POINT; FBP = FINAL BOILING POINT.

30–60 mesh activated clay. The object of clay filtration is to remove by adsorption nonionic (oil soluble) surfactants and other impurities. Removal of surfactants helps meet WSIM specifications for removal of oil fields chemicals, corrosion inhibitors finding their way in kerosene feed, and incomplete removal of naphthenate in Merox feed pretreatment. Thermal stability of the product is also improved by removal of impurities and organometallic copper compounds and other colored molecules formed as a result of oxidation of naphthenates due to excess air or temperature.

The Merox-treated product is superior to other chemically treated products, because it is free from copper, lead, and elemental sulfur. Merox-treated jet fuel is superior to hydrotreated product with respect to the product's lubricity and stability.

### NOTES

- 1. C. D. Lowry, Jr. *Plumbite Sweetning of Gasoline*. Universal Oil Product Co., Booklet 242, May 1940.
- 2. W. L. Nelson. *Petroleum Refinery Engineering*, 4th ed. New York: McGraw-Hill, 1964.