Chemical Treatment of Petroleum Products

The aims of chemical treatment is to remove the impurities, such as sulfur, nitrogen, oxygen, asphaltene, unsaturated compounds and some aromatics compounds at low temperature. Treatment processes for the removal of impurities compounds are much less severe than the hydrotreating processes. In fact, it is generally recognized that the removal or conversion of theses compounds in distillates by treatment processes is usually limited to the lower molecular weight compounds.

Methods of Chemical Treating

1- Oxidative Processes
2- Caustic Processes
3- Acid Processes
4- Solvent Processes, having three types
   - Solvent Deasphalting
   - Solvent extraction
   - Solvent dewaxing

1- Oxidative Processes

Oxidative treatment processes are, in fact, processes that have been developed to convert the objectionable-smelling mercaptans to the less-objectionable disulfides by oxidation. However, disulfides tend to reduce the tetraethyl lead susceptibility of gasoline, and recent trends are toward processes that are capable of completely removing the mercaptans. These reactions are carried out on the light products (such as gasoline and kerosene) because the mercaptans are concentrated within these cuts.

There are many methods for oxidative treating (for example, Bender process, Copper Sweetening Process, Doctor Process, Hypochlorite Sweetening Process, Merox Process).

Merox Process

Merox is a proprietary catalytic chemical process for mercaptans oxidation developed by UOP used in oil refineries and natural gas processing plants to remove mercaptans from LPG, propane, butanes, light naphthas, kerosene and jet fuel by converting them to liquid hydrocarbon disulfides.

Processes within oil refineries or natural gas processing plants that remove mercaptans and/or hydrogen sulfide (H₂S) are commonly referred to as sweetening processes because they result in products which no longer have the sour, foul odors of mercaptans and hydrogen sulfide. The liquid hydrocarbon disulfides may remain in the sweetened products, they may be used as part of the refinery or natural gas processing plant fuel, or they may be processed further. The Merox process is usually more economical than using a catalytic hydrodesulfurization process for much the same purpose.

Types of Merox Process Units

UOP has developed many versions of the Merox process for various applications:

- Conventional Merox for extraction of mercaptans from LPG, propane, butanes or light naphthas.
- Conventional Merox for sweetening jet fuels and kerosenes.
- Merox for extraction of mercaptans from refinery and natural gases.
- Minalk Merox for sweetening of naphthas. This process continuously injects just a few ppm of caustic into the feed naphtha.
- Caustic-free Merox for sweetening jet fuels and kerosenes. This process injects small amounts of ammonia and water (rather than caustic) into the feed naphtha to provide the required alkalinity.
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In all of the above Merox versions, the overall oxidation reaction that takes place in converting mercaptans to disulfides is:

$$4 \text{RSH} + \text{O}_2 \rightarrow 2\text{RSSR} + 2\text{H}_2\text{O}$$

**Conventional Merox for Sweetening Jet Fuel or Kerosene**

The conventional Merox process for the removal of mercaptans (i.e., sweetening) of jet fuel or kerosene is a one-step process. The mercaptan oxidation reaction takes place in an alkaline environment as the feedstock jet fuel or kerosene, mixed with compressed air, flows through a fixed bed of catalyst in a reactor vessel. The catalyst consists of charcoal granules that have been impregnated with UOP's proprietary catalyst. The oxidation reaction that takes place is:

$$4 \text{RSH} + \text{O}_2 \rightarrow 2\text{RSSR} + 2\text{H}_2\text{O}$$

The jet fuel or kerosene sweetening process also requires that the feedstock be prewashed to remove any H$_2$S that would interfere with the sweetening. The reaction that takes place in the batch caustic prewash vessel is:

$$\text{H}_2\text{S} + \text{NaOH} \rightarrow \text{NaSH} + \text{H}_2\text{O}$$

**Diagram**

![Diagram of Conventional Merox process unit for sweetening jet fuel or kerosene](image-url)
The Merox reactor is a vertical vessel containing a bed of charcoal granules that have been impregnated with the UOP catalyst. An alkaline environment is provided by caustic being pumped into reactor on an intermittent, as needed basis.

The jet fuel or kerosene feedstock from the top of the caustic prewash vessel is injected with compressed air and enters the top of the Merox reactor vessel along with any injected caustic. The mercaptan oxidation reaction takes place as the feedstock percolates downward over the catalyst. The reactor effluent flows through a caustic settler vessel where it forms a bottom layer of aqueous caustic solution and an upper layer of water-insoluble sweetened product. The caustic solution remains in the caustic settler so that the vessel contains a reservoir for the supply of caustic that is intermittently pumped into the reactor to maintain the alkaline environment.

The sweetened product from the caustic settler vessel flows through a water wash vessel to remove any entrained caustic as well as any other unwanted water-soluble substances, followed by flowing through a salt bed vessel to remove any entrained water and finally through a clay filter vessel. The clay filter removes any oil-soluble substances, organometallic compounds (especially copper) and particulate matter, which might prevent meeting jet fuel product specifications.

The pressure maintained in the reactor is chosen so that the injected air will completely dissolve in the feedstock at the operating temperature.

### 2-Caustic Processes

The process consists of mixing a water solution of lye (sodium hydroxide or caustic soda) with a petroleum fraction. The treatment is carried out as soon as possible after the petroleum fraction is distilled, as contact with air forms free sulfur, which is very corrosive and difficult to remove. The lye reacts with any hydrogen sulfide present to form sodium sulfide, which is soluble in water.

There are many methods for caustic process (such as Dualayer Process, Mercapsol Process, Polysulfide Treatment, Sodasol Process, Unisol Process)

#### Unisol Process

The Unisol process is a regenerative method for extracting not only mercaptans but also certain nitrogen compounds from sour gasoline or distillates. The gasoline, free of hydrogen sulfide, is washed countercurrently with aqueous caustic-methanol solution at about 40°C (100°F). The spent caustic is regenerated in a stripping tower (145°C to 150°C, 290°F to 300°F), where methanol, water, and mercaptans are removed.

### 3- Acid Treatment

Treating petroleum products with acids is, like caustic treatment. Various acids, such as hydrofluoric acid, hydrochloric acid, nitric acid, and phosphoric acid, have been used in addition to the more commonly used sulfuric acid, but in most instances there is little advantage in using any acid other than sulfuric.

#### Sulfuric Acid Treatment

Sulfuric acid treatment is a continuous or batch method that is used to remove sulfur compounds. The treatment will also remove asphaltic materials from various refinery stocks. The acid strength varies from fuming (>100%) to 80%; approximately 93% acid finds the
most common use. The weakest suitable acid is used for each particular situation to reduce sludge formation from the aromatic and olefin hydrocarbons. The use of strong acid dictates the use of a fairly low temperature (-4°C to 10°C, 25°F to 50°F), but higher temperatures (20°C to 55°C, 70°F to 130°F) are possible if the product is to be redistilled.

4- **Solvent Treating**
Distillation splits a mixture into fractions according to the boiling points of the mixture constituents. In contrast, solvent refining segregates compounds with similar compound types, such as paraffins and aromatics. The three main types of solvent refining are solvent deasphalting, solvent extraction, and solvent dewaxing.

**Solvent Deasphalting**
Solvent deasphalting takes advantage of the fact that aromatic pounds are insoluble in paraffins. Propane deasphalting is commonly used to precipitate asphaltenes from residual oils. Deasphalted oil (DAO) is sent to hydrotreaters, FCC units, hydrocrackers, or fuel-oil blending. In hydrocrackers and FCC units, DAO is easier to process than straight-run residual oils. This is because asphaltenes easily form coke and often contain catalyst poisons such as nickel and vanadium, and the asphaltene content of DAO is (by definition) almost zero.

In traditional solvent deasphalting, residual oil and propane are pumped to an extraction tower at 150 to 250°F (65 to 120°C) and 350 to 600 psig (2514 to 4240 kPa). Separation occurs in a tower, which may have a rotating disc contactor (Figure below). Liquid products are evaporated and steam stripped to recover the propane solvent, which is recycled.

An advanced version of solvent deasphalting is “residuum oil supercritical extraction (ROSE),” In this process, the oil and solvent are mixed and heated to above the critical temperature of the solvent, where the oil is almost totally insoluble. Advantages include higher recovery of deasphalted liquids, lower operating costs due to improved solvent recovery, and improved energy efficiency. The ROSE process can employ three different solvents, the choice of which depends upon process objectives:

- **Propane**: Preparation of lube base stocks
- **Butane**: Asphalt production
- **Pentane**: Maximum recovery of liquid
Solvent Extraction
Solvent extraction is used to remove aromatics and other impurities from lube and grease stocks. The feedstock is dried, then contacted with the solvent in a counter-current or rotating disk extraction unit (Figure above). The solvent is separated from the product stream by heating, evaporation, or fractionation. Remaining traces of solvent are removed from the raffinate by steam stripping or flashing. Electrostatic precipitators may be used to enhance separation of inorganic compounds. The solvent is then regenerated and recycled. Today, phenol, furfural, and cresylic acid are widely used as solvents. In the past, some refiners installed the Edeleanu process, in which the solvent is liquid sulfur dioxide, but the hazards of potential leaks made it undesirable. Chlorinated ethers and nitrobenzene also have been used.

Solvent Dewaxing
Solvent dewaxing removes wax (normal paraffins) from deasphalted lube base stocks. The main process steps include mixing the feedstock with the solvent, chilling the mixture to crystallize wax, and recovering the solvent. Commonly used solvents include toluene and methyl ethyl ketone (MEK). Methyl isobutyl ketone (MIBK) is used in a wax deoiling process to prepare food-grade wax.