Merox and Related Metal Phthalocyanine Catalyzed Oxidation Processes

B. Basu a, S. Satapathy a & A. K. Bhatnagar a
a Indian Oil Corporation Limited, Research and Development Center, Sector-13, Faridabad, 121007, India


To cite this article: B. Basu, S. Satapathy & A. K. Bhatnagar (1993): Merox and Related Metal Phthalocyanine Catalyzed Oxidation Processes, Catalysis Reviews: Science and Engineering, 35:4, 571-609

To link to this article: http://dx.doi.org/10.1080/01614949308013917

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.
Merox and Related Metal Phthalocyanine Catalyzed Oxidation Processes

B. BASU, S. SATAPATHY, and A. K. BHATNAGAR

Indian Oil Corporation Limited
Research and Development Center
Sector-13, Faridabad—121007, India

I. INTRODUCTION .................................................. 572
II. PROCESS DESCRIPTION ........................................ 573
   A. Feed Preparation ........................................... 573
   B. Merox Extraction ........................................... 573
   C. Merox Sweetening .......................................... 575
   D. Combined Operation ...................................... 578
III. CATALYSTS ..................................................... 579
   A. Merox and Related Processes ............................. 579
   B. Purification of Gaseous Streams ......................... 581
   C. Preparation of Metal Phthalocyanines .................. 584
IV. PROMOTERS ..................................................... 586
   A. Chemicals Used as Promoters ............................. 586
   B. Mechanism of Promotion .................................. 589
V. CATALYST COMPOSITES ....................................... 590
   A. Adsorbents .................................................. 590
   B. Preparation of Catalyst Composite ....................... 593
   C. Reactivation of Catalyst Composite ..................... 594
VI. EVALUATION OF CATALYSTS ................................. 594
VII. MECHANISM OF CATALYTIC ACTION ....................... 595

Copyright © 1993 by Marcel Dekker, Inc.
I. INTRODUCTION

Alkyl and aromatic mercaptans are among important organic sulfur compounds distributed in petroleum products. The mercaptans cause foul odor and are corrosive toward metals. In addition, mercaptans may cause oxidative deterioration as well as inhibit the performance of various additives (TEL, antioxidants) in finished products. Therefore, it is necessary to remove them, either by extractive processes or by converting them into innocuous disulfides. Such processes are usually referred to as "sweetening."

There are many commercially viable sweetening processes, which are listed in Table 1 [1]. One such process, viz., Merox, developed by UOP Inc. in 1958, is perhaps most popular and is used worldwide. Merox is an efficient and economical catalytic process developed for the chemical treatment of petroleum fractions for removal of sulfur present as mercaptans (Merox extraction) or direct conversion of mercaptans to disulfides (Merox sweetening). It is used for liquid-phase treating of liquified petroleum gas (LPG), natural gas liquids (NGL), naphthas, gasolines, kerosenes, jet fuels, diesel fuels, and heating oils. It can also be used to sweeten natural gas, refinery gas, and synthetic gas in combination with conventional pretreatment and posttreatment processes [2].

There is an enormous literature on Merox and similar catalytic processes from UOP as well as from other groups of workers in various countries. In recent years, much work was done on understanding the mechanism of mercaptan oxidation by metal chelates similar to Merox catalysts which also mimic certain biological processes. However, the subject has not been

<table>
<thead>
<tr>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caustic wash</td>
</tr>
<tr>
<td>Doctor treatment</td>
</tr>
<tr>
<td>Hypochlorite wash</td>
</tr>
<tr>
<td>Solutizer and Dualayer processes</td>
</tr>
<tr>
<td>Copper chloride sweetening</td>
</tr>
<tr>
<td>Inhibitor sweetening</td>
</tr>
<tr>
<td>Sulfuric acid treating</td>
</tr>
<tr>
<td>Vapor-phase clay treatment</td>
</tr>
<tr>
<td>Molecular sieves</td>
</tr>
<tr>
<td>Chelate sweetening</td>
</tr>
<tr>
<td>Merox process</td>
</tr>
<tr>
<td>Mercapfining</td>
</tr>
<tr>
<td>Hydrofining/hydrotreating</td>
</tr>
<tr>
<td>Lead sulfide sweetening</td>
</tr>
<tr>
<td>Unisol treating</td>
</tr>
<tr>
<td>Bender–Petreco</td>
</tr>
<tr>
<td>Merifining</td>
</tr>
</tbody>
</table>
reviewed extensively in recent years. The aim of the present review is to fulfill this objective.

II. PROCESS DESCRIPTION

The Merox process is based on the ability of a metal chelate to catalyze the oxidation of mercaptans to disulfides in alkaline medium. The reaction proceeds at an economically practical rate at or near normal refinery product downstream (run-down) temperatures and pressures. For light distillates, operating pressure is controlled slightly above the bubble point to ensure liquid-phase operation. For heavier stocks, the operating pressure is set to keep desired stoichiometry of air dissolved in the reaction mixture. Gases are usually treated at their prevailing system pressure [2].

The processes of Merox extraction and sweetening can be used singly or in combination depending upon the feed mercaptan type, its content, and finished product specification. The essential steps of the Merox process are described below.

A. Feed Preparation

The feed, before Merox sweetening/extraction, is often given a mild caustic wash. The purpose of such pretreatment is to remove hydrogen sulfide, lower mercaptans, and acidic catalyst toxins or toxin precursors, which increases the efficiency of the process and enhances catalyst life. Carlson [3, 4] reported caustic wash for the removal of naphthenic acids followed by percolation through activated charcoal to remove catalyst toxins and toxin precursors. Percolation through a charcoal bed was found to be effective for the removal of phenols from sour petroleum distillates [5]. Percolation through a weakly basic anion exchange resin (Amberlyst A-21) [6] for the partial removal of mercaptans and substantial removal of catalyst toxins and toxin precursors was also reported. For color-degradable feeds, sweetening was limited to mercaptan oxidation by controlling the dissolved oxygen in feed by nitrogen purging [7].

B. Merox Extraction

The mercaptans are extracted by an aqueous solution of caustic soda according to Eq. (1).

\[
RSH + \text{NaOH} \rightleftharpoons \text{NaSR} + \text{H}_2\text{O}
\]

\text{(oil)} \quad \text{(aqueous)} \quad (1)

The process reduces the total sulfur content in the finished product and is suitable for treating gases, LPG, and light gasoline fractions.

Reaction (1) is reversible, and with increasing molecular weight of
mercaptans there is a sharp fall in the conversion into mercaptide (Table 2) [8]. The forward reaction is favored by low temperature, low molecular weight of mercaptans, and high caustic concentration.

In mercaptan extraction units [2] (Fig. 1), fresh feed is charged to an extraction column in which mercaptans are extracted by a countercurrent caustic stream. The treated product passes overhead to storage or downstream processing. The mercaptan-rich caustic solution containing Merox catalyst flows from the bottom of the extraction column to the regenerator section through a steam heater. Air is injected into this stream, and the mixture flows upward through the oxidizer, where caustic is regenerated by conversion of mercaptans to disulfides. The oxidizer effluent flows into the disulfide separator, where spent air, caustic-entrained hydrocarbons, disulfide oil, and regenerated caustic solution are separated. Separation of caustic from disulfide oil is promoted by the addition of naphtha [9]. The regenerated caustic stream is returned to the extraction column. Successive

<table>
<thead>
<tr>
<th>Mercaptan</th>
<th>Boiling point, °C</th>
<th>Relative distribution coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>7</td>
<td>213.0</td>
</tr>
<tr>
<td>Ethyl</td>
<td>37</td>
<td>80.0</td>
</tr>
<tr>
<td>n-Propyl</td>
<td>67</td>
<td>10.7</td>
</tr>
<tr>
<td>n-Butyl</td>
<td>97</td>
<td>3.0</td>
</tr>
<tr>
<td>n-Amyl</td>
<td>126</td>
<td>1.0</td>
</tr>
</tbody>
</table>

**TABLE 2**

*Extraction of Mercaptans with Caustic Soda*

FIG. 1. Merox mercaptan extraction unit. E, extractor; O, oxidizer; DS, disulfide separator; -- --- -- --, intermittent use.
extraction and regeneration steps decrease the concentration of caustic solution, which in turn lowers the extraction efficiency. Increase in the concentration of caustic has been achieved by contacting a portion of the alkali solution with a warm hydrocarbon stream [10].

The regenerated caustic contains small quantities of disulfides which are picked up by the finished product. Presence of small amounts of disulfides usually does not interfere with the finished product specification except in cases when finished streams are further catalytically treated. In such cases, regenerated caustic is made sulfur-free by single or repeated extraction with naphtha [11], or a part of the processed stream [12]. Removal of disulfides has also been reported by catalytic hydrogenation or by electrochemical reduction [13].

Extraction of mercaptan-rich caustic before regeneration for the removal of olefins and acetylenes during the processing of olefinic hydrocarbons has been reported [14]. This helps in limiting the level of oxygenates in the finished product.

The kinetics of mercaptan absorption by potassium hydroxide was examined by Sokolina et al. [15]. The authors also reported mass transfer equations for the extraction of ethyl mercaptan from hydrocarbons by 20% KOH [16]. Clonts [17] described a superior process for mercaptan extraction by 25% caustic in an extractor packed with stainless steel fiber bundles. Similar fiber bundle packed columns have been used for the catalytic regeneration of mercaptan-rich caustic [18]. Mercaptan extraction processes similar to Merox were also reported by LaFoy [12], Adamis [19], and Mazgarov et al. [20–22].

C. Merox Sweetening

Sweetening is achieved by blowing caustic/hydrocarbon mixture with air in the presence of a catalyst. Mercaptans are oxidized into disulfides [Eq. (2)] [1] which remain dissolved in the product. There is no reduction in the total sulfur content of the finished product.

\[
2\text{NaSR} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{RSSR} + 2\text{NaOH} \tag{2}
\]

There are three versions of Merox sweetening (Figs. 2, 3, and 4) [2]. These are liquid–liquid, fixed-bed, and fixed-bed using minute amounts of caustic (Minalk). These versions are described below.

Liquid–Liquid Sweetening (Fig. 2) [2]. Hydrocarbon feed, air, and aqueous caustic soda containing dispersed Merox catalyst are simultaneously contacted in a mixing device, where mercaptans are converted to disulfides. Mixer effluent is directed to a settler, from which the treated hydrocarbon stream is sent to storage. Separated caustic solution from the settler is recirculated to the mixer. A small amount of Merox catalyst is added periodically to maintain the catalytic activity.

The liquid–liquid sweetening process is applicable for feeds containing
FIG. 2. Liquid–liquid Merox sweetening unit. M, Merox; CS, caustic settler; ---, intermittent use.

FIG. 3. Fixed-bed Merox sweetening unit. R, reactor; CS, caustic settler; ---, intermittent use.

easily oxidizable mercaptans, for example, virgin (straight-run) and light thermally cracked gasolines, and catalytically cracked gasolines.

**Fixed-Bed Sweetening (conventional)** (Fig. 3). Fixed-bed sweetening is used for treating virgin streams or cracked feedstocks having final boiling points beyond 140°C, viz., kerosene, jet fuel, diesel, and heating oils. The high molecular weight and more branched mercaptans associated with these stocks are sparingly soluble in caustic and are difficult to oxidize. The fixed-bed process, which provides longer contact and residence time, is suitable for the oxidation of such mercaptans.

The fixed-bed sweetening units consist of a reactor containing an activated charcoal bed impregnated with Merox catalyst and wetted with caustic solution. Feed and air are passed through the reactor, during which the mercaptans are oxidized to disulfides. The treated stream is directed to a settler for the separation of feed and caustic. Separated caustic is circulated intermittently to keep the catalyst bed wet. In an improved sweetening process, separated caustic was percolated through a charcoal bed [23] to remove surface-active impurities. This maintained the activity of the catalyst bed for a longer time.

The fixed-bed process was modified to lower the equipment and operation cost while maintaining the same high efficiency as the original process. In the process termed “Merox Minalk” [2] (Fig. 4), a small amount of dilute caustic is continually injected into the feed before it passes through the catalyst bed. The dilute caustic provides necessary alkalinity for mercaptan oxidation. The process is useful for feeds that are easy to sweeten, such as virgin and catalytically cracked naphthas.

In another process, a fixed-bed reactor and a caustic settler were integrated into the same unit [24]. The feed and caustic, after passing through the catalyst bed, flowed through a cylindrical screen into an annular separation zone which surrounded the lower part of the catalyst bed. Separation of caustic from feed took place in this zone. Maple et al. [25] reported a dual-stage sweetening process in two oxidation zones within the same reactor. In the first oxidation zone the feed was contacted with caustic and air over a fiber bundle and then reacted over a fixed-bed catalyst system. A simultaneous process for sweetening and extraction was described by Asdigian [26] in which feed and caustic were contacted countercurrent in a contacting column while a limited amount of air was injected at an intermediate point of the contacting zone. Thus, the upper zone acted as a sweetening section while the lower section functioned as extractor.

The finished product may be given further treatment to remove residual mercaptans and disulfides. Addition of N-(cyclohexylthio)-N-phenyl benzenesulfonamide [27] was found to be effective for the removal of trace levels of mercaptans after sweetening of sour kerosene containing >4000 ppm of mercaptans. Washing with spent sulfuric acid [28] from alkylation was reported for the reduction of disulfide content of the treated stock.

Degassing of the finished product for dissolved nitrogen and oxygen
at reduced pressure [29, 30] was recommended for reducing safety hazards and emission problems during storage.

D. Combined Operation

The combined process is applicable for lighter distillates (gasoline, naphtha) containing higher levels of mercaptans. The advantage of this process is that it can perform the dual function of extracting easily removable mercaptans and converting the remaining mercaptans to disulfides.

In a typical Merox combination process (Fig. 5) [31], feed is prewashed with caustic before being contacted by catalyst and caustic in the extractor. Feed is then settled and air is injected before it is passed into the Merox sweetener. The treated product is then settled again for caustic separation and taken to storage.

In the regeneration step, caustic is pumped from the bottom of the extractor and mixed with air in the oxidizer. Disulfides and excess air are separated from the regenerated caustic, which is recirculated to the top of the extractor.

The combined process was used for simultaneous treating of a low- and high-boiling feedstocks [32, 33]. The feeds were extracted by caustic in two extractors, and the spent alkalis from extractors were combined for regeneration in a common oxidizer. A part of the regenerated caustic was then used for sweetening high-boiling feed and the separated caustic was recirculated to extractor. A combination of liquid–liquid sweetening followed by percolation through a charcoal bed and fixed-bed sweetening was reported by Carlson et al. [4] for treating feeds containing mercaptans that are difficult to oxidize, catalyst toxins, and toxin precursors.

FIG. 5. Combined Merox process. O, oxidizer; E, extractor; CP, caustic prewash; CS, caustic settler; R, reactor.
III. CATALYSTS

A. Merox and Related Processes

In the Merox process, mercaptans are oxidized to disulfides in alkaline medium in the presence of a metal phthalocyanine catalyst [34]. Such phthalocyanines may include cobalt [34], iron [13], manganese [35, 36], molybdenum [37], and vanadium [7, 37] phthalocyanine. The preferred phthalocyanine is either cobalt or vanadium [24, 38–45], with cobalt being especially preferred. A mixture of phthalocyanines such as cobalt and manganese [35] has also been used as catalyst.

In general, metal phthalocyanines are not soluble in aqueous medium and, therefore, for improved catalytic activity, it is necessary to convert them into water-soluble derivatives [34]. This may be achieved by either sulfonation or carboxylation of phthalocyanines. In Merox catalysts, sulfonated cobalt phthalocyanines are used. The degree of sulfonation may be 1, 2, or 4.

Cobalt phthalocyanine monosulfonate is used as the principal component in Merox sweetening catalyst and there are a large number of examples indicating its use. Some of the references indicating use include patents filed on behalf of UOP by Strong [23], Hillman [46], Stansky [47, 48], Carlson [3, 5, 6, 49–56], and Frame [40, 57–65]. The monosulfonated derivatives are preferred because the higher sulfonated derivatives are more soluble in water, which causes their leaching away from the catalyst bed. However, the use of cobalt phthalocyanine disulfonate [66], tetrasulfonate [67], and a mixture of mono- and disulfonate [68] as sweetening catalyst has also been reported.

In Merox extraction, highly sulfonated metal phthalocyanines are used as catalyst due to their better solubility in aqueous medium compared to monosulfonated derivatives. Cobalt phthalocyanine tetrasulfonate [35, 45, 69] is the preferred catalyst, although the use of its vanadium [45, 69], manganese [35], and molybdenum [45] analogs has also been reported.

Besides UOP Inc., several other companies have used metal complexes of phthalocyanines and phthalocyanine analogs as catalyst for mercaptan removal processes. Interestingly, water-insoluble phthalocyanines, cobalt phthalocyanine, and its derivatives were also used as catalysts.

The use of phthalocyanine for catalytic oxidation of mercaptans in cracked naphtha [70, 71] and sour kerosene [72] was reported. The catalyst was used either as a suspension in caustic or supported on a composite. Cobalt phthalocyanine supported on activated carbon was used for the regeneration of mercaptan-rich caustic [73] as well as for sweetening sour distillates [25]. Mazgarov et al. [74] reported the catalytic demercaptanization of hydrocarbon feedstocks by brominated cobalt phthalocyanine on a porous support. Maizlish et al. [75] and Anan’eva et al. [76] described a process for preparing a catalyst system with increased activity by mixing...
cobalt phthalocyanine, or its tetrachloro or tetramethyl derivative, with a thermoplastic polymer, and then molding and extruding the same in a suitable shape and size. Oxidation of ethyl mercaptan to disulfide in presence of phenoxy-substituted cobalt phthalocyanines [77] in 1% aqueous caustic was also reported in a German patent.

Conventional Merox catalysts, viz., sulfonated cobalt phthalocyanines, were applied for mercaptan oxidation processes, notably by Russian workers. Mazgarov et al. [20, 21] reported the use of disodium cobalt phthalocyanine disulfonate in caustic for oxidation of mercaptans in low-boiling distillate fractions. Voltsov et al. [28] used the same catalyst for the sweetening of broad hydrocarbon fractions. The promoting action of glycols in catalytic activity of disulfonated cobalt phthalocyanine was established by Fomin et al. [78] in model experiments with ethyl, propyl, and isopropyl mercaptan. Simultaneous catalytic oxidation of hydrogen sulfide and butyl mercaptan by disulfonated cobalt phthalocyanine was studied by Mazgarov et al. [79]. It was reported that small additions of sodium sulfide increased the rate of sodium butyl mercaptide oxidation up to a certain concentration while addition of sodium butyl mercaptide decreased the rate of sodium sulfide oxidation. Maizlish et al. [80] reported that the brominated amino, hydroxy, nitro, or sulfo derivatives of cobalt phthalocyanine were more effective catalysts than their corresponding nonbrominated analogs. In a diesel fuel, up to 97% of the mercaptans were removed by using cobalt octabromo-octahydroxy phthalocyanine, compared to only 14% removal in presence of cobalt phthalocyanine disulfonate. In a Romanian patent [81], efficient removal of mercaptans in gasoline was described by using cobalt phthalocyanine disulfonate as catalyst. Complete desulfurization of a propane–propylene stream containing 0.13% mercaptans in the presence of a mixed cobalt and copper phthalocyanine sulfonates was also reported by Romanian authors [82].

Catalytic applications of highly substituted cobalt phthalocyanines were described by various authors. A stable catalyst composition in aqueous slurry or suspension form consisting predominantly of di- and tetrasulfonated cobalt phthalocyanine was described by Dowd [83]. Presence of a highly soluble tetrasulfonated derivative eliminated the precipitation and gelation problems associated with disulfonate slurries. Cobalt phthalocyanine tetrasulfonate supported on anion-exchange resins [84] was reported as an efficient catalyst for oxidation of mercaptans in aqueous or nonaqueous systems. Catalytic applications of mono- or polysulfonated cobalt phthalocyanine, and mono- or polycarboxylated cobalt phthalocyanine were described in a French patent [85]. Mercaptan removal from low- and high-boiling fractions based on cobalt phthalocyanine sulfonamide catalyst and mercuric chloride as promoter was reported in Indian patents [86, 87]. The authors, on the basis of laboratory and plant evaluation, observed that cobalt phthalocyanine containing 3 to 4 sulfonamide groups could be used as an effective liquid/liquid sweetening catalyst [88] for low-boiling fractions. Metal phthalocyanines in
which the metal atom is also bonded to axial ligands [89] were found to be useful for the oxidation of mercaptans to disulfides as well as organic sulfides to elemental sulfur. For example, added butyl mercaptan in a kerosene feed was converted to elemental sulfur in the presence of oxoethoxo(phthalocyanato 4-sulfonic acid) molybdenum supported on activated charcoal.

Catalytic applications of highly complex metal phthalocyanines, viz., cobalt or vanadium chelates of 2,9,16,23-tetrakis(3,4-dicarboxybenzoyl) phthalocyanine were patented by Clifford of Ashland Oil Inc. [90–92]. The catalysts were effective for mercaptan oxidation in homogeneous (caustic) as well as heterogeneous (charcoal bed) systems.

Metal phthalocyanines in their polymeric forms [87, 93, 94] were also used as catalysts in mercaptan oxidation processes though to a lesser extent, probably due to their excessive cost [78] (~50 times more than their monomeric forms). The catalytic activities of polynmetallophthalocyanines were reported to be higher [78, 95–97] than their monomers. Denisova et al. [96, 97] studied catalytic oxidation of a series of mercaptans in the presence of cobalt and iron phthalocyanines, and reported that oligomeric forms of catalysts and supported catalysts were more active than the unsupported monomeric ones. Buck et al. [98] evaluated the activities of polymeric nickel, cobalt, and iron phthalocyanines for 2-mercaptoethanol oxidation and observed that their activities were in the order of Co >> Fe >> Ni. Sulfonamide-substituted polynmetallophthalocyanines [87] and a combination of cobalt polyphthalocyanine and cobalt polybutylmercaptide [99] were used for sweetening petroleum fractions.

Metal chelates of various phthalocyanine analogs were reported for their catalytic activity. Applications of cobalt tetraphenylporphyrin sulfonates for mercaptan oxidation in liquid-liquid extraction [19] and solid-bed sweetening [100] processes were reported by Adamis and co-workers. Sweetening of sour petroleum distillates in the presence of cobalt or vanadium chelates of tetrapyridinoporphyrazine was described by Anderson and Ward [101]. Oxidation of substituted aromatic mercaptans by a tetraaza(14)annulene-cobalt complex was studied by Sakata et al. [102] and it was observed that the corresponding nickel complex was inactive. Possible catalytic applications of cobalt porphyrin, cobalt corrin, and chelates of the general formula ML or M(LH₂)X₂—where M is a transition metal, X is an anion, and L is from a tetradeutentate ligand based on the diamide of picolinic acid or its derivatives—was reported by Mimoun et al. [85]. Interestingly, a simple metal chelate such as cobalt phthalate, in conjunction with ephedrine and betaine [103], was used for treating sour petroleum distillates in liquid-liquid or fixed-bed processes.

B. Purification of Gaseous Streams

Cobalt phthalocyanine and its derivatives were used in catalytic processes for the removal of hydrogen sulfide and lighter mercaptans from
various gaseous streams such as refinery waste gas, fuel gas, natural gas, etc. Such processes, in addition to purification of gaseous streams, also led to the recovery of elemental sulfur while oxidizing hydrogen sulfide. In a process patented by UOP [104] for the purification of gaseous streams, H$_2$S and CO$_2$ were initially removed by absorption in aqueous sodium or potassium carbonate solution. Hydrogen sulfide picked up by the circulating carbonate solution was then oxidized by cobalt phthalocyanine, elemental sulfur was removed, and the stream was stripped to remove CO$_2$. In another process [105], H$_2$S present in a CO$_2$-rich gaseous stream was oxidized in the presence of air and water over a fixed-bed catalyst containing cobalt phthalocyanine disulfonate. Grover and Nagji described a process [106] for the removal of CO$_2$, H$_2$S, and mercaptans from gaseous C$_1$ to C$_8$ streams. In this process, the gaseous feed was initially contacted with an adsorbent for the partial removal of H$_2$S and mercaptans, followed by contacting with aqueous alkaline medium for substantial purification of the treated gas.

Applications of cobalt phthalocyanines for the catalytic removal of H$_2$S from gaseous streams were also reported in Russian literature. Vasilievskaya and Golyand [107] studied conditions for the removal of H$_2$S from waste gases by using sulfonated cobalt phthalocyanine and observed that 95% to 98% H$_2$S could be removed from air containing 2 g H$_2$S/m$^3$. The efficiencies of other metal phthalocyanines were 50% to 60% under the same conditions. Mazgarov et al. [79] evaluated conditions for simultaneous oxidation of H$_2$S and mercaptans by cobalt phthalocyanine disulfonate. Kinetics of H$_2$S oxidation in alkaline medium in presence of disulfonated cobalt phthalocyanine and polymeric cobalt phthalocyanine [108, 109] catalysts were investigated in detail. The authors reported that increase in concentration of catalyst increased the oxidation rate and yield of sulfur, while increasing the temperature increased the thiosulfate formation instead of sulfur. Agaev et al. [110] reported that by passing natural gas through alkaline solution containing polymeric cobalt phthalocyanine or sulfonated cobalt phthalocyanine at 20° to 35°C, all mercaptans and H$_2$S were completely removed. The enthalpy, entropy, and activation energy of H$_2$S oxidation in presence of polymeric cobalt phthalocyanine were 5.2 Kcal/mole, 19.2 units, and 5.8 Kcal/mole, respectively, whereas in presence of sulfonated cobalt phthalocyanine, the values were 6.6, 17.9, and 7.2, respectively, indicating higher activity of polymeric catalyst. Kuliev and co-workers [111] also reported the optimum conditions for purification of natural gas containing 300 to 400 mg/m$^3$ of light mercaptans in presence of polymeric cobalt phthalocyanine catalyst.

A process for substantial removal of H$_2$S from shale processing generator gas was described by Afanas'ev et al. [112], in which H$_2$S was stripped by aqueous sodium carbonate in a horizontal hollow absorber. The spent solution was regenerated concurrently by air in the presence of sulfonated cobalt phthalocyanine while elemental sulfur and sodium thiosulfate were recovered from the top of the reactor. Regeneration of H$_2$S-rich absorbent
by air blowing at 20° to 30°C in presence of active carbon supported cobalt polyphthalocyanine catalyst [113] was also reported. Catalyst prepared by fusion of finely dispersed cobalt phthalocyanine into a polymer support was reported to be highly durable and chemically stable in aqueous-alkaline medium [114]. Such catalysts were suitable for the treatment of Na₂S-containing alkaline wastewater and for demercaptanization of light hydrocarbon materials. Treatment of sulfide-containing wastewater by catalytic oxidation in the presence of tetrasulfonated cobalt phthalocyanine was also reported by Chinese workers [115].

A new method for the removal of H₂S and SO₂ from Claus tail gases by a single-stage absorption–catalytic oxidation process was described by Fomin et al. [116]. The process was based on the oxidation of H₂S by SO₂ and oxygen in the presence of a catalyst system containing cobalt phthalocyanine disulfonate, dimethylformamide or dimethylacetamide, water, and dimethylaminopropanenitrite as promoter. The elemental sulfur produced in the process was suitable for reuse.

Besides H₂S and mercaptan removal processes, metal phthalocyanines were also used for the catalytic oxidation of chemical contaminants. In an interesting example, Hong et al. [117] reported the preparation of a hybrid catalyst system by linking cobalt tetraaminophthalocyanine and cobalt tetrasulfophthalocyanine to the surfaces of a chemically modified silica gel, a functionalized titanium oxide, and an amino-substituted macroporous polymer. The catalyst was suitable for aqueous-phase oxidation of N₂H₄, H₂S, SO₂, and mercaptans. In another example, Kitajima et al. [118] reported the use of cobalt phthalocyanineoctacarboxylate supported on γ-alumina as an exhaust gas catalyst for the removal of aldehydes, alcohols, and mercaptans.

Metal phthalocyanines were also explored as industrial deodorants useful for purifying industrial waste gases and air by decomposing ammonia, amines, hydrogen sulfide, and mercaptans. The preparation of such deodorant compositions was described in a series of Japanese patents [119–126] which essentially consisted of loading a metal phthalocyanine on a suitable polymeric support. Various metal phthalocyanines used as catalyst in deodorant compositions include iron phthalocyaninecarboxylic acids [120, 121, 125, 126], cobalt phthalocyaninesulfonic acids [122, 123], cobalt phthalocyanineoctaamine [119], and iron phthalocyaninetetra thiocyanate [124]. For catalyst support, usually nonwoven fabrics were used—such as wool [122, 123], viscose rayon [120, 121], acrylic fibers [119], poly(vinyl alcohol) fibers [124], and nylon 6 [125]. The catalyst composites were prepared by soaking the fibers for 5 to 24 h in aqueous acidic (pH 2–4) solution of the catalyst, followed by washing and drying. In another example, the authors [126] prepared the catalyst system by polymerizing cobalt phthalocyanine carboxylic acid, terephthalic acid, and ethylene glycol at 200°C for 5 h. The resulting polymer containing cobalt phthalocyanine exhibited high efficiency even after 1 year of continuous use.
C. Preparation of Metal Phthalocyanines

The phthalocyanines, especially copper phthalocyanine, are considered as an important class of pigments for their outstanding properties of brightness and strength combined with fastness to light, heat, and chemicals. The two original methods of manufacture of these pigments [127]—viz., (i) the phthalic anhydride–urea process and (ii) the phthalonitrile process—are still considered to be the only technically important alternatives. However, a considerable amount of effort has been expended throughout the world on modification and refinement of these two processes.

Reviewing methods of phthalocyanine synthesis is outside the scope of the present work. However, a few of the references connected with the preparation of metal phthalocyanines as catalysts for mercaptan oxidation processes are discussed here.

1. Phthalic Anhydride–Urea Process

Standard conditions of this process involve heating a mixture of phthalic anhydride (4 moles), urea (16 moles), metal salt (1 mole), and a catalytic amount of ammonium molybdate in a high-boiling solvent such as kerosene, nitrobenzene, or trichlorobenzene [Eq. (3)].

\[
\text{C}_6\text{H}_4\text{O} + \text{H}_2\text{NCONH}_2 + \text{MX}_2 \xrightarrow{\text{Solvent, Catalyst}} \text{MPc}
\]

(3)

Here, Pc represents the phthalocyanine anion \((\text{C}_{32}\text{H}_{16}\text{N}_3^{2-})\) (Fig. 6) and \(\text{M}^{2+}\) represents the metal ion.

![Phthalocyanine molecule](image)
2. Phthalonitrile Process

In the phthalonitrile process, metal phthalocyanines are manufactured by heating phthalonitrile with an appropriate amount of metal salts as such, or in the presence of an organic base (e.g., pyridine) as solvent [Eq. (4)].

\[ \text{C}_6\text{H}_4(\text{CN})_2 + \text{MX}_2 \rightarrow \frac{\text{Neat (300°C)}}{\text{Solvent (180°C)}} \rightarrow \text{MPc} \]

3. Sulfonation of Phthalocyanines

Simple sulfonic acids, viz., \(\text{CuPc(SO}_3\text{H})_n\) where \(n = 1, 2, 3,\) or 4, are made by the oleum sulfonation of phthalocyanines [127]. The sulfonation can be controlled to give a range of derivatives with sulfonic acid mainly entering in the 3-(α-) position. Cobalt phthalocyanine was partially sulfonated to contain 15% to 40% of the monosulfonic acid, in 10% oleum under mild conditions to give the vat dye Indanthrene Brilliant Blue 4G [127]. Cobalt phthalocyanine monosulfonate was also prepared [128, 129] by the reaction of 4-sulfophthalic acid, cobalt sulfate, ammonium molybdate, and urea, followed by addition of this mixture to phthalic anhydride and heating for 6 h. Kupriyanova et al. [130] reported the preparation of a catalyst for \(\text{H}_2\text{S}\) oxidation by sulfonation of phthalic anhydride followed by neutralization and subsequent reaction with cobalt and molybdenum salts, and urea.

The disulfonic acid of cobalt phthalocyanine was claimed to be best prepared by sulfonation in an inert atmosphere [127]. The sulfonation was performed either by concentrated sulfuric acid for 8 h at 120°C, or by oleum at 20°C to 30°C for 26 h, under carbon dioxide atmosphere. The preparation of disodium cobalt phthalocyanine sulfonate by sulfonation of cobalt phthalocyanine with sulfur trioxide in an inert atmosphere was reported [131] to be improved in the presence of sodium chloride. Cobalt phthalocyanine tetra-4-sulfonic acid was prepared by Fukada [132] from the ammonium salt of 4-sulfophthalic acid by the urea process, and the same method was used by him for the preparation of tetrasulfonic acids of other transition metal phthalocyanines [133]. The same method was also used by Douglas [134] for the preparation of cobalt phthalocyanine tetrasulfonic acid.

The preparation of cobalt phthalocyanine sulfonamides was reported by Agrawal et al. [88]. The method involved reaction of cobalt phthalocyanine with chlorosulfonic acid to yield its sulfonyl chloride, which was then converted to amide by interacting with ammonia or amines. The degree of substitution of cobalt phthalocyanine was reported to be between 3 and 4.

4. Carboxylation of Phthalocyanines

Carboxylated derivatives of metal phthalocyanines were prepared [135] by reacting them with trichloroacetic acid, or by the action of phosgene and
aluminum chloride. In the second method the acid chlorides were initial products which upon hydrolysis resulted in carboxylic acids.

Preparation of highly carboxylated metal phthalocyanines—viz., 2,9,16,23-tetrakis(3,4-dicarboxybenzoyl) cobalt phthalocyanine was reported in patents from Ashland Oil Inc. The method [90, 91] involved heating 3,3′,4,4′-benzophenonetetracarboxylic dianhydride, urea, cobalt chloride, boric acid, and ammonium molybdate in trichlorobenzene, followed by the separation and neutralization of the product with caustic to give the octasodium salt of the cobalt complex.

5. Polymeric Phthalocyanines

Phthalocyanines exist in various polymeric forms. Preparation of such polymers was described by Moser et al. [136]. Preparation of polymetallophthalocyanines involved heating a mixture of tetracyanobenzene, urea, and metal chloride [136–138]. Insoluble crosslinked metal complexes as well as soluble metal complexes with framework terminal groups were obtained by varying the polymerization condition.

Interestingly, synthesis of metal phthalocyanines on the surface of catalyst support was also reported [139]. For this, the catalyst support was impregnated with metal chloride solution followed by fusion of the impregnated support with phthalic anhydride and urea in the presence of ammonium molybdate at 180–200°C for 3–4 h. Synthesis of monomeric and polymeric cobalt phthalocyanine derivatives on the surfaces of supports such as silica, alumina, and charcoal was also reported by Woehrle et al. [95].

IV. PROMOTERS

The efficiency of the Merox process is increased by the incorporation of certain chemicals in the cobalt phthalocyanine/activated charcoal composite (sweetening) or in the caustic solution containing the catalyst (sweetening/extraction). The presence of such chemicals, termed "promoters," also increases the catalyst life.

A large number of compounds including organic bases, alcohols, acids, and a few inorganic salts have been used as promoters. Brief descriptions of such chemicals are given below.

A. Chemicals Used as Promoters

1. Alcohols

The mercaptan extraction process by aqueous caustic is promoted by the use of compounds that increase the solubility of mercaptans in the aqueous phase. Of these, methanol, as used in the Unisol process, was
reported to be most effective [1]. The promoting action of methanol as solubilizer in the Merox fixed-bed sweetening process [23, 39] was also reported.

Besides methanol, glycols and cresols were also used as promoters in mercaptan extraction processes. Fomin et al. [78, 140] reported the use of di- or triethylene glycols, while in another Russian publication [141], C₆-H₂₂ poly(ethylene glycol) was effectively used. Aqueous caustic containing 30% of cresols as solubilizer [142] was effectively used for the extraction of mercaptans from kerosene. The effectiveness of solubilizers increased in the order of p-cresol, mixture of o- and p-cresol, and mixed cresols.

2. **Acetic Acid**

It has been reported that the inclusion of a small amount of acetic acid [50, 53, 54] in the cobalt phthalocyanine/activated charcoal composite (referred to further as “catalyst composite”) resulted in a superior catalyst.

3. **Morpholine**

Carlson et al. [52, 55, 143] have reported the promoting action of morpholine. The compound at the 5- to 50-ppm level was either impregnated on the catalyst composite [55, 143] or doped in the sour feed [52].

4. **Urea**

The catalyst composite impregnated with urea [51, 144] was claimed to be particularly effective for the sweetening of feedstocks containing difficult-to-oxidize mercaptans.

5. **Ethanolamine**

Mazgarov et al. [21, 22, 145] have reported that the efficiency of mercaptan extraction by caustic was enhanced by the presence of ethanolamine. The use of ethanolamine complex formed with Group I, VI, and VII metal bromides [145] was reported as promoter for the oxidation of mercaptans in spent caustic.

6. **Naphthalene Sulfonic Acids**

The catalyst composite containing 7-amino-1,3-naphthalenedisulfonic acid [57, 60] showed improved activity and longer life than the conventional catalyst composite (without promoter). The superior performance of a catalyst composite impregnated with 2-hydroxy-6-naphthalene sulfonic acid was also reported.

7. **Alternate Bases**

Alternate bases other than caustic have been used with advantage in Merox or similar processes. Stansky [47, 48] has reported the use of alcoholic
tetramethyl guanidine to enhance the efficiency of the sweetening process. Additionally, use of tetramethyl guanidine simplified the processing of distillate fractions, especially ATF, as the treated stream did not require subsequent caustic removal steps.

It has been reported [48] that sweetening in the presence of ammonium hydroxide as alternate base was of low effectiveness. Nevertheless, Frame et al. [146] achieved effective sweetening of sour fluid catalytically cracked gasoline (FCC gasoline) by ammonia in the presence of catalyst composite impregnated with quaternary ammonium salts as promoter. UOP licences a process in which ammonia is used in place of caustic in the Minalk process for sweetening FCC gasoline. The process, termed "caustic-free Merox," requires a more active catalyst (Merox 21) and a catalyst promoter (Merox CF). The presence of ammonia during sweetening was found to enhance the catalyst life [65, 147]. Promoting action of triethylamine and pyridine for the oxidation of ethyl mercaptan was reported by Prakhov et al. [148]. In China, a process for the alkali-free sweetening with activator (AFSA) has been developed [149] for refining primary distillation products, such as gasoline, kerosene, diesel, and cracked gasoline containing a large amount of higher molecular weight mercaptans. In the process, a trace quantity of the activator (5–20 ppm) is mixed with the hydrocarbon stream before sweetening over a fixed-bed catalyst containing cobalt phthalocyanine.

It was observed that sweetening of sour kerosene by catalyst composite in presence of tetramethylammonium hydroxide [150] as base was more effective compared to sodium methoxide. Sour petroleum distillates were sweetened to a doctor-sweet product in the presence of trimethyl(hydroxyethyl) ammonium hydroxide [59, 61]. The catalyst bed was initially wetted with quaternary ammonium hydroxide and was then subsequently added to the catalyst bed at 12-h intervals admixed with the sour feed. Frame [39, 42, 151] has reported the use of benzyldimethylalkylammonium hydroxide under similar conditions for the sweetening of sour petroleum distillates. However, for feeds containing mercaptans that are difficult to oxidize, the presence of caustic [41] was also required for efficient sweetening. The quaternary ammonium hydroxide compound, under such condition, functioned as promoter.

Oxidation-resistant mercaptans in petroleum distillates were sweetened in the presence of sodium isopropoxide [152] as base, which was dissolved in excess (about 5 times more than the mercaptan content) in the sour feed.

8. Quaternary Ammonium Compounds

The use of quaternary ammonium hydroxides and their analogs as effective promoters has been widely claimed in a series of patents filed by UOP Inc. in the last decade. The efficiency of the sweetening process, especially for distillates containing difficult-to-oxidize mercaptans, was in-
increased by the incorporation of benzyldimethylalkyl ammonium hydroxide [41, 44, 45, 153, 154] (alkyl: a mixture [41, 45] of C\textsubscript{12}, C\textsubscript{14}, C\textsubscript{16}, and C\textsubscript{18} chain lengths) in the catalyst composite. The efficiency of the sweetening process was further increased by using a combination of benzyldimethylalkyl ammonium hydroxide and a surfactant, viz., sodium lauryl sulfate [44, 45, 154].

Quaternary ammonium salts, usually in the form of chlorides, were also used as promoters. The promoting action of benzyldimethylalkyl ammonium chloride [38, 43, 62–66, 155, 156] was reported in a number of UOP patents. Sweetening of sour FCC gasoline by using a mixture of benzyldimethylalkyl ammonium chloride and benzylmethyldialkyl ammonium chloride as promoter, and ammonium hydroxide as alkaline agent, was reported by Frame et al. [146]. The applications of relatively simpler compounds such as ethanoltrimethylammonium chloride [58] and triethylbenzylammonium chloride [157] as promoters were also reported.

9. Miscellaneous

The incorporation of onium compounds—such as phosphonium, arsenium, oxonium, sulfonium, and stibonium compounds—in catalyst composites to promote the oxidation of mercaptans was reported by Bricker et al. [158]. Pollastrini et al. [103] have used cobalt phthalate as catalyst in combination with betaine and ephedrine as promoters for the sweetening of sour petroleum distillates.

The use of inorganic salts for increasing the efficiency of mercaptan oxidation by phthalocyanine catalysts has also been reported. Examples of such promoters include alkali metal sulfates, chlorides, nitrates, carbonates, acetates, benzoates [159], sodium sulfide [79], lead mercaptides [70], and mercuric chloride [87].

B. Mechanism of Promotion

The mechanism of promoting action of various compounds listed above has not been covered effectively in the literature. However, the promoting action of certain compounds (alcohols, glycols, and cresols) has been attributed to their ability to solubilize mercaptans in the aqueous phase [1]. A similar theory based on phase-transfer catalysis can perhaps be advanced for explaining the mechanism of another major class of promoters, viz., quaternary ammonium compounds. Such types of compounds are well-known phase-transfer catalysts and their mechanism of action has been discussed by Gokel et al. [160]. Based on this, it can be theorized that during the oxidation of mercaptans in hydrocarbon—aqueous alkaline solution system, the quaternary ammonium cation (Q\textsuperscript{+}) exchanges for the cation associated with the nucleophilic reagent salt (NaSR). The new re-
agent, \( Q^+SR^- \), dissolves in the organic phase and undergoes oxidation in the presence of cobalt phthalocyanine catalyst.

V. CATALYST COMPOSITES

The Merox process is operated with the catalyst maintained in homogeneous (extraction, liquid–liquid sweetening) as well as heterogeneous (fixed-bed sweetening) conditions. In the homogeneous processes the catalyst is conveniently dispersed in caustic solution (5–15°Be) whereas, in the heterogeneous process, it is essential to maintain the catalyst in the form of a solid composite (catalyst bed) in the reactor. The catalyst composite consists of a suitable adsorbent which is impregnated with the cobalt phthalocyanine catalyst and usually with a promoter. The role of the adsorbent is to provide support to the catalyst molecules in such a manner that they are uniformly available throughout the composite matrix for mercaptan oxidation. It has been established [95] that the catalyst dispersed homogeneously over a carrier has considerably higher activity than the unsupported one.

A. Adsorbents

In the Merox fixed-bed sweetening process, activated charcoal (10 × 30 mesh) has been found to be most suitable as catalyst support. A large number of patents from UOP Inc. [3, 23, 30, 36, 40, 41, 44, 50–66, 68] report applications of activated charcoal as catalyst support and as adsorbent for catalyst toxins and toxin precursors in feed preparation. Such charcoals were derived from wood, lignite coal, bituminous coal, peat, and petroleum. A typical specification of activated charcoal is listed in Table 3 [4].

Activated carbon [25, 77, 81, 94, 113] and carbon black [80, 161] have

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area</td>
<td>600 m²/g</td>
</tr>
<tr>
<td>Density</td>
<td>0.40–0.45 g/cc</td>
</tr>
<tr>
<td>Bed density</td>
<td>235 lb/ft³</td>
</tr>
<tr>
<td>Sieve analysis</td>
<td></td>
</tr>
<tr>
<td>% retained on No. 12 sieve</td>
<td>5</td>
</tr>
<tr>
<td>% through No. 30 sieve</td>
<td>5</td>
</tr>
<tr>
<td>Uniformity coefficient</td>
<td>1.7 or less</td>
</tr>
<tr>
<td>Abrasion % retention</td>
<td>75 min</td>
</tr>
<tr>
<td>Ash content</td>
<td>17%</td>
</tr>
<tr>
<td>Moisture content</td>
<td>6%</td>
</tr>
</tbody>
</table>
been used as catalyst support in metal phthalocyanine catalyzed sweetening processes similar to the Merox process. Claude et al. [162, 163] have used a catalyst composite containing cobalt phthalocyanine (0.05–10%), pyrolytic carbon (5–35%), and mineral matrix (60–90%) for the sweetening of sour petroleum distillates.

Catalyst composite containing weakly basic anion exchange resin (Amberlyst A21) as carrier [164–167] was found to be resistant toward deactivation by gum formation. The resin also exhibited better attrition resistance than conventional charcoal-supported catalyst and reduced the gum content of the treated feed. Another anion-exchange resin (Sephadex DEAE A25 or A50) was also evaluated as carrier by Skorobogaty et al. [84].

Carlson has reported the advantageous use of a molecular sieve [43] and alumina [67] as catalyst support. Incorporation of a molecular sieve as desiccant in the conventional activated charcoal based catalyst also resulted in a superior catalyst [36].

It has been observed by Woehrle et al. [95] that the catalytic activity, related to the metal phthalocyanine content, increased with increased dispersion of catalyst on carrier. In this connection, the influence of carrier on catalytic activity was found to be highest for activated charcoal [95, 168], followed by alumina and silica. Prakhov et al. [148] correlated the catalytic activity with the electron-donating ability of the support and observed that the catalytic activity decreased in the following order: ion-exchange resin (Amberlyst A21) > activated charcoal > zinc oxide > silica.

1. Polymeric Adsorbents

A novel class of bifunctional catalysts composed of cobalt phthalocyanine tetrasodiumsulfonate coordinately bound to a polymeric base was developed mainly by Brouwer et al. [169–177] and by Schutten et al. [178, 179]. Cobalt phthalocyanine tetrasulfonate (CoPcTS) bound to poly(vinylamine) was used extensively for studying various aspects of the mercaptan oxidation process [169–179]. The water-soluble catalyst system showed enzyme-like behavior [169, 174] and exhibited considerably higher activity [174, 176] than the unbound CoPcTS. CoPcTS bound to poly(vinylamine–vinyl alcohol) copolymer [175] was evaluated, and an increase in intrinsic activity of the catalytic sites was observed with increasing ethylamine (base group) content of the polymer. Poly(vinylamine) CoPcTS catalyst system was crosslinked with α,α'-dichlororoxylene [171], yielding porous hydrophilic networks in the same. Reaction rates of mercaptan oxidation for these immobilized catalyst systems appeared to be 4 to 30 times lower as compared with the water-soluble polymeric catalyst system but still higher than those of polymer-free catalyst. However, no loss in catalytic activity of poly(vinylamine)–cobalt phthalocyanine system was observed when it was bound to macroporous divinylbenzene–styrene copolymer [179].

The catalytic activity of CoPcTS bound to poly(ethylenimine), poly(1-
lysine), and ionenes [poly(quaternary ammonium hydroxide)] [176, 177] (Fig. 7) was also studied for the oxidation of 2-mercaptoethanol. All these ligands, including poly(vinylamine), enhanced the reaction rate considerably in comparison with their monomeric analogs. The catalysts exhibited similar behavior toward the effect of salt and pH. For ionenes [177] the reaction rates increased virtually linearly with a linear charge density on ligands, which is consistent with the earlier reported [175] findings on vinylamine and vinylalcohol copolymer. Three main parameters provided the enhanced polycationic effect: (i) high linear charge density on the polymer, (ii) large amount of base groups in the polymer domain, and (iii) low ionic strength for the reaction solution. Furthermore, a comparison of linear charge density, catalytic activity, and activation parameters for the ionene catalysts with those obtained earlier with vinylamine–vinylalcohol copolymer showed that the presence of hydrophilic side groups had a promoting effect on the oxidation of hydrophilic mercaptans. From catalyst reuse experiments, it was observed that the polyamine catalysts had poor stability whereas ionenes could be used many times.

A photometric method was developed by Van Streun et al. for the determination of molecular weight of 2,4-ionenes by attaching a chromophoric moiety to the end groups [180]. The method was used for investigating the effects of molecular weight of 2,4-ionenes on the oxidative coupling of 2-mercaptoethanol in the presence of CoPcTS. Monomeric analogs of 2,4-ionenes showed no increase of reaction rate as compared with the polymer-free system. However, relatively low molecular weight ionene ($M_n = 1740$) showed a dramatic increase in the reaction rate. The structural behavior of CoPcTS was investigated in the presence of ionenes by using visible light spectroscopy [181]. The promoting action of ionenes was attributed to the enhancement of aggregation of cobalt complex.

Van Herk et al. [182] have reported the immobilization of polymeric catalyst [CoPcTS–poly(quaternary ammonium salt)] on latex particles by using soap-containing quaternary ammonium compounds. Using the latex-supported polymeric catalysts, the activity of its homogeneous counterpart could be maintained while at the same time immobilization was accom-
plished. In another study by Hassanein et al. [183, 184], CoPcTS was bound to cationic latexes prepared from styrene, divinylbenzene, and surface-active monomer, and used as a catalyst for the oxidation of 1-decylmercaptan. The higher activity of the colloidal CoPcTS latexes than that of CoPcTS was attributed primarily to the absorption of 1-decylmercaptan by the latexes, which provided a higher concentration of reactant at the active sites [184]. The authors suggested that the oxidation of many other organic compounds in water could be strongly catalyzed by transition metal catalysts bound to polymer latexes. Shirai et al. [185] observed that cobalt phthalocyanine tetracarboxylic acid covalently bound to 2-vinylpyridine–styrene copolymer, despite being a heterogeneous system, was a remarkably effective catalyst for mercaptan oxidation because of polymer effects. The catalytic activities of polypeptide-wrapped unsubstituted cobalt and iron phthalocyanines [186] have been used for studying the oxidation of 2-mercaptoethanol. The polypeptides consisted of L-lysine, L-glutamic acid, and β-alanine. Higher catalytic activity was observed with higher content of L-lysine.

In Russian literature, heterogeneous catalysts prepared by fusion of finely dispersed cobalt phthalocyanine or its water-insoluble derivatives into thermoplastic polymers [75, 76, 114, 187], were reported as effective sweetening catalysts. Such catalysts were highly durable and chemically stable in aqueous alkaline media.

B. Preparation of Catalyst Composite

The homogeneous catalyst system used in Merox extraction and the liquid–liquid sweetening process is prepared by dispersing the cobalt phthalocyanine sulfonate catalyst and promoter in aqueous caustic solution. The fixed-bed catalyst for the Merox sweetening process is prepared by impregnating cobalt phthalocyanine sulfonate catalyst and promoter on activated charcoal or any other suitable adsorbent. The catalyst and promoter are conveniently dispersed/dissolved in a suitable medium including methanol [50, 54, 56, 60, 61], isopropanol [188], monoethanolamine and water [189], water [51, 55], ammonia [41, 44, 45], and caustic [113, 155, 164]. The impregnation is carried out by circulating a solution or dispersion of catalyst and promoter through the activated charcoal bed [40, 41, 44, 62, 188] till the circulating solution becomes almost colorless. Alternatively, the charcoal bed is initially contacted with the promoter solution, and the resulting composite is dried and contacted again with the catalyst solution [60, 155]. The catalyst bed is dried and wetted with aqueous caustic prior to the commencement of the sweetening operation. The catalyst bed may initially be treated with steam and inert gas for 2 to 6 h at 430°C to 530°C, followed by drying under inert atmosphere [49], for better impregnation of the catalyst.

In another process, the catalyst composite is prepared by soaking,
suspending, or mixing [51, 53, 54, 61, 144, 164, 165] the adsorbent in a solution of catalyst and promoter for a desired length of time. The mixture is then evaporated to dryness. The composite may be further dried at ambient temperature or at an elevated temperature in an oven, or in a flow of hot gas. In a superior method, the adsorbent is immersed in an impregnating solution/dispersion in a rotary evaporator and tumbled for 1 h [40, 41, 62, 188]. The catalyst composite is then dried after the removal of solvent.

In an interesting study, the impregnation of activated charcoal with Merox catalyst solution in ammonia or methanol was simulated by Leitao et al. [190, 191] using a heterogeneous model with pore diffusion in particles. The simulation showed that in industrial impregnation processes involving circulation of Merox catalyst solution through the activated charcoal bed, only 15% of the bed held the catalyst. Washing of the catalyst bed after impregnation slightly improved the catalyst distribution.

C. Reactivation of Catalyst Composite

Merox liquid catalyst composite is reactivated by percolation through an adsorbent (activated charcoal, γ-alumina) bed followed by addition of further quantities of metal phthalocyanine sulfonates in the recovered catalyst solution [37, 69].

The conventional reactivation of Merox fixed-bed catalyst includes washing the charcoal support with water and acetic acid at 90° to 175°C to remove caustic, gums, and hydrocarbons; treating the washed charcoal with steam at 340° to 530°C; and reimpregnating the charcoal with a solution of metal phthalocyanine complex [46]. The catalyst beds that do not respond to conventional regeneration techniques can be regenerated by sequential treatment with water at 75° to 100°C followed by an aqueous solution of benzylidimethylalkylammonium hydroxide-type promoters [44, 45, 192]. Optionally, the catalyst bed may be impregnated with aqueous ammoniacal solution containing cobalt phthalocyanine monosulfonate [193] alone or in combination with sodium laurylsulfate [43, 44] prior to the promoter treatment.

VI. EVALUATION OF CATALYSTS

The effectiveness of various catalysts and promoters has been evaluated either by simple laboratory experiments or by carrying out the sweetening operation in a bench-scale fixed-bed reactor. Such evaluations were mostly carried out with sour petroleum distillates [6, 38, 39, 50, 51, 54, 59–61, 143, 150, 164], containing known amount of mercaptans. Alternatively, standard solutions of various mercaptans—viz., butyl mercaptan [79, 89–92, 191], decyl mercaptan [183, 184], ter-dodecyl mercaptan [52], and thio-
phenol [35, 36, 92]—were used. The effectiveness of cobalt phthalocyanines bound to polymeric ligand-type catalysts was evaluated with respect to water-soluble 2-mercaptoethanol [169, 172, 175, 177, 178, 194]. The catalysts and promoters were usually evaluated in the form of solid composites, that is, impregnated over activated charcoal.

The laboratory evaluation of catalysts (alone or in combination with promoters) was performed by shaking a mixture of sour feed, catalyst composite, and caustic in a stoppered flask. The shaking was performed either manually for a short duration of 5 min [48, 150, 164, 166] or for a longer duration ranging from 30 to 120 min [6, 50, 52–55, 81] in a mechanical shaker, depending upon the complexity and concentration of mercaptans in the feed. In another series of experiments, the catalysts were evaluated by bubbling air [88, 90, 91] through a mixture containing catalyst composite, sour feed, and caustic in a glass vessel, and monitoring the mercaptan level in feed with time. Similar experiments under pressure in a glass-lined reactor [195] were also reported. Various experimental parameters such as feed-to-catalyst ratio, catalyst-to-promoter ratio, air flow rates, etc., were kept constant in a particular series of experiments.

The evaluation of catalysts and promoters in a fixed-bed vertical tubular reactor [38, 39, 44, 51, 58–61, 63, 143, 162] has been reported in a large number of publications. During such experiments, the reactor was packed with the solid catalyst composite. The feed was percolated from the top of the reactor, usually at a liquid hourly space velocity of 0.5 h\(^{-1}\) under air pressure of 45 psig [38, 39, 58–61, 63]. The catalyst bed was wetted intermittently with caustic or promoter solution at fixed intervals. The mercaptan content in the sweetened distillate was monitored from time to time. The layout of a fixed-bed sweetening apparatus has been described by Shcherbachenko et al. [196]. Evaluation of catalytic activity by monitoring the oxygen uptake [35, 184] during mercaptan oxidation reaction was also reported.

**VII. MECHANISM OF CATALYTIC ACTION**

Metal phthalocyanines and metalloporphyrins have been reported as highly effective catalysts for many chemical reactions [136]. Iron phthalocyanine [197] has long been known to exhibit a high catalase activity as well as activity in the oxidation reactions involving certain cyclic and aromatic (benzaldehyde, tetralin, diphenylmethane, cyclohexane) compounds. The catalytic activity of iron, cobalt, and nickel phthalocyanines for the oxidation of a host of organic compounds has been documented in the literature [136]. It has been established that nickel phthalocyanine was also catalytically active for the oxidation of saturated ketones, fatty acids, and alkyl aromatic compounds. Kropf and co-workers [198–201] have studied the mechanism
of oxidation of cumene with oxygen in the presence of metal phthalocyanines, many of which turned out to be effective catalysts.

It was reported earlier that in metal phthalocyanine catalyzed oxidation of hydrogen sulfide, mercaptans, and amino acids, the central atom of the metal complex plays a dominant role [202, 203]. In such reactions, only iron and cobalt phthalocyanines were found to be catalytically active. Vasilievskaya et al. [107] have studied the catalytic oxidation of hydrogen sulfide by metal phthalocyanines and observed that the catalytic activity of various metal phthalocyanines decreased in the order of Co > V > Mn > Fe > Sn > Ni > Cu. Very recently, Shirai et al. [185] have examined the oxidation of 2-mercaptoethanol in the presence of iron, nickel, and cobalt phthalocyanines containing 2, 4, and 8 carboxylic acid groups. It was observed that the metal ion and the number of carboxylate ions affected the catalytic activity. Cobalt and iron phthalocyanines containing 4 and 8 carboxylate groups were found to be remarkably effective whereas nickel and copper phthalocyanine carboxylates were less active. Buck et al. [98] have reported the activities of nickel, cobalt, and iron polymeric phthalocyanines (average degree of polymerization: 10) for 2-mercaptoethanol oxidation as 70, 630, and 420 moles of substrate/mole of catalyst/min, respectively (Table 4). Various aspects of the mechanism of metal phthalocyanines catalyzed reactions and the role of the central atom during their catalytic action have been discussed in detail by Berezin [204].

The presence of substituents in the phthalocyanine ring also affects its catalytic activity. Titova and co-workers [205, 206] have determined the first-order rate constants and activation energies for the oxidation of 2-benzothiazolethiol with tetranitro, tetramino, and tetrahydroxy derivatives of cobalt phthalocyanine disulfonate, and cobalt phthalocyanine tetrasulfonate as catalysts. It was observed that electron-donating substituents increased the activity of the catalyst. In a similar study, Lazovenko et al. [207] have reported tetrahydroxy-substituted cobalt phthalocyanine disulfonate as the most active catalyst for the oxidation of 2-benzothiazolethiol. Maizlish et al. [80] have reported that the brominated amino, hydroxy, nitro, or sulfo derivatives of cobalt phthalocyanine were more effective catalysts for oxidation of mercaptans than their corresponding nonbrominated analogs. The catalytic activity of octabromo-octahydroxy cobalt phthalocyanine was found to be roughly 7 times higher than cobalt phthalocyanine disulfonate for the sweetening of sour diesel fuel. Heundorf et al. [168] have also reported that the presence of electron-donating substituents in cobalt phthalocyanines increased their catalytic activity, whereas electron-withdrawing substituents decreased their activity (Table 4).

The rate of oxidation of mercaptans depends on their structural complexity as well (Table 4). The 50-fold greater rate of oxidation [147] of n-dodecylmercaptan in presence of cobalt phthalocyanine adsorbed on a mineral oxide support compared to that of ter-dodecylmercaptan under the same conditions was attributed to steric hindrance. Denisova et al. [96] have
### TABLE 4
Influence of Central Atom, Substituent, and Substrate on the Catalytic Activity of Metal Phthalocyanines

<table>
<thead>
<tr>
<th>Phthalocyanine type</th>
<th>Catalytic activity</th>
<th>Substrate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Central atom</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monomeric</td>
<td>Co &gt; V &gt; Mn ≧ Fe &gt; Sn &gt; Ni &gt; Cu.</td>
<td>H₂S</td>
<td>[107]</td>
</tr>
<tr>
<td>Monomeric</td>
<td>Co &gt; Fe ≧ Ni &gt; Cu.</td>
<td>2-Mercaptoethanol</td>
<td>[185]</td>
</tr>
<tr>
<td>Polymeric</td>
<td>Co &gt; Fe &gt; Ni.</td>
<td>2-Mercaptoethanol</td>
<td>[98]</td>
</tr>
<tr>
<td>Substituent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cobalt</td>
<td>Generally, electron-donating substituents increased the activity.</td>
<td>2-Benzothiazolethiol</td>
<td>[205–207]</td>
</tr>
<tr>
<td>Cobalt and iron</td>
<td>Activity increased with the number of carboxylic groups. Octacarboxy ≧ tetracarboxy ≧ dicarboxy.</td>
<td>Ethyl mercaptan</td>
<td>[168]</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Brominated derivatives more active than nonbrominated ones.</td>
<td>2-Mercaptoethanol</td>
<td>[185]</td>
</tr>
<tr>
<td>Substrate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cobalt and iron</td>
<td>CH₃</td>
<td>Sour diesel</td>
<td>[80]</td>
</tr>
<tr>
<td></td>
<td>n-C₄H₉SH &gt; C₂H₅—CHSH &gt; (CH₃)₂—CHCH₂SH &gt; C₆H₁₃SH &gt; HSCH₂—CH—COOH</td>
<td>—</td>
<td>[96]</td>
</tr>
<tr>
<td>Cobalt</td>
<td>n-C₁₂H₂₅SH ≧ i-C₁₂H₂₅SH</td>
<td>—</td>
<td>[147]</td>
</tr>
</tbody>
</table>
studied the oxidation of $n$-butyl mercaptan, sec-butyl mercaptan, isobutyl mercaptan, $n$-hexyl mercaptan, and cysteine in presence of various monomeric and polymeric metal phthalocyanines, and have observed that activity of the substrates decreased in the stated order.

The mechanism for the oxidation of mercaptans in alkaline medium in the presence of transition metal complexes was published by Wallace et al. [208] in 1964. The authors suggested the following reaction scheme:

$$
\text{RSH} + \text{NaOH} \rightarrow \text{RS}^- + \text{Na}^+ + \text{H}_2\text{O} \quad (5)
$$

$$
2\text{M}^{2+} + \text{O}_2 \rightleftharpoons 2\text{M}^{3+} + \text{O}_2^{2-} \quad (6)
$$

$$
2\text{RS}^- + 2\text{M}^{3+} \rightarrow 2\text{M}^{2+} + 2\text{RS}' \quad (7)
$$

$$
2\text{RS}' \rightarrow \text{RSSR} \quad (8)
$$

$$
\text{O}_2^{2-} + \text{H}_2\text{O} \rightarrow 2\text{OH}^- + \frac{1}{2}\text{O}_2 \quad (9)
$$

The scheme involves the activation of molecular oxygen by metal catalyst followed by the reaction of catalyst with substrate to produce RS' radical. The kinetics of oxidation of ethyl mercaptan in the presence of catalysts (copper salts, cobalt phthalocyanine tetrasulfonate) was studied by Lescinskaite et al. [209], and it was observed that each catalyst had its own optimum pH and temperature range. In a recent publication, kinetic data for the oxidation of butyl mercaptan and hydrogen sulfide were interpreted according to the above reaction scheme by Ovsyannikova et al. [210]. The oxidation mechanism of mercaptans in a hydrocarbon–aqueous alkaline solution system was reported to be different [211] from that in a homogeneous phase (alkaline solution only). The reaction rate determining step in the heterogeneous oxidation was the diffusion transfer of mercaptans from the oil phase into the aqueous phase. Consequently, the heterogeneous reaction rate constant decreased with increasing length of the carbon chain in the mercaptan molecule.

Leitao and Rodrigues [191, 195] have studied the kinetics of oxidation of butyl mercaptan in heptane in the presence of caustic for simulation of the fixed-bed Merox process and for subsequent designing of a Merox reactor. Oxidation in the presence of caustic without catalyst, in the presence of unsupported catalyst, in the presence of activated carbon, and in the presence of supported catalyst was examined and corresponding rate laws were formulated. The work was extended [212] to the oxidation of $n$-hexyl mercaptan and to the sweetening of a typical light gasoline. The kinetic model formulated for the oxidation of $n$-butyl mercaptan in the presence of supported Merox catalyst was tested for the interpretation of sweetening experiments of a light gasoline. It was observed that the model predicted the experimental data reasonably well. The simulation of a typical Merox reactor was then performed. The fixed-bed reactor was modeled by using a one-dimensional heterogeneous plug-flow model. Both the steady-state and transient behavior were studied, as well as the influence on the
simulation results of the real distribution of Merox catalyst inside particles and along the bed. The influence of catalyst distribution on simulation results was found to be small for the oxidation of n-butyl mercaptan but higher for the more difficult-to-oxidize mercaptans.

In recent years it has been suggested that in metal phthalocyanine catalyzed oxidation of mercaptans, mercaptide anion acts as a ligand and that (by ligand exchange) direct oxidation to disulfide occurs in the complex. Kinetics of cysteine oxidation catalyzed by cobalt phthalocyanine tetrasulfonate (CoPcTS) has been studied [213] by the polarographic method. The kinetic equation derived indicated that the reaction followed a mechanism involving the formation of an intermediate ternary complex [CoPcTS (cys) (O$_2$)] that probably contained a second cysteine as RS' radical on the macrocyclic ligand. Kinetics and mechanism of the reduction of CoPcTS by 2-mercaptoethanol under anoxic conditions were investigated by Leung et al. [214]. The authors suggested that the catalyst in the form of dimer participated in the oxidation reaction involving two steps. The first step was

$$\text{Co(II)PcTS} + \text{RS}^- \rightleftharpoons \text{RS}^-\text{Co(II)PcTS}_2$$  \hspace{1cm} (10)

$$\text{RS}^-\text{Co(II)PcTS}_2 \rightarrow \text{Co(II)PcTS} + \text{Co(I)PcTS} + \text{RS}^-$$  \hspace{1cm} (11)

a rapid equilibrium complexation of the cobalt(II) phthalocyanine tetrasulfonate dimer with mercaptide anion (RS$^-$), while the second rate-determining step involved electron transfer from the bound mercaptide to the Co(II). The products of the two-step mechanism were assumed to be the mixed cobalt(I) and cobalt(II) phthalocyanine tetrasulfonate dimer and mercaptide radical (RS'). Mercaptide radical further reacted to form disulfide.

The authors [215, 216] have further studied the mechanism of oxidation of 2-mercaptoethanol in the presence of CoPcTS catalyst. The proposed reaction scheme was essentially similar to the reduction of CoPcTS catalyst under anoxic condition and involved three main steps. The steps included binding of the dimeric catalyst with molecular oxygen, followed by the complexation of the substrate by oxygenated dimer, and then subsequent electron-transfer steps. The electron transfer from the Co(II) metal center to bound oxygen was found to be the rate-determining step. The proposed reaction mechanism was supported by evidence obtained from a large number of experiments. Kinetic data indicated a mechanism that proceeded via a dimeric catalytic center, bridged by the mercaptide anion. The binding of molecular oxygen has been found to precede the binding of mercaptide anion, which in turn stabilized the Co(II)--oxygen bond. ESR and magnetic susceptibility data suggested the formation of superoxide-like cobalt complexes during the course of catalytic oxidation. This evidence indicated the complex [RS$^-\text{Co(II)PcTS}\text{RS}^-\text{Co(III)PcTS}\text{O}_2^-]$ as the prin-
Principal reactive species in the catalytic cycle (Fig. 8). The formation of RS' radical was demonstrated by the production of ascorbate radical, and the formation of another intermediate, hydrogen peroxide, was confirmed by fluorescence studies. The overall stoichiometry of mercaptan oxidation as suggested by the authors is given below:

\[
\begin{align*}
2\text{RSH} + \text{O}_2 &\rightarrow \text{RSSR} + \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + 2\text{RSH} &\rightarrow \text{RSSR} + 2\text{H}_2\text{O}
\end{align*}
\]

(12) (13)

Shirai et al. [185] have also reported that the oxidation of mercaptans catalyzed by tetra- and octasubstituted metal phthalocyanines proceeded via the formation of ternary activated complex in which RS⁻ and molecular oxygen reversibly coordinate with the central metal on the phthalocyanine rings. However, the catalyst cobalt phthalocyanine octacarboxylate participated as monomer due to the electrostatic repulsion of negatively charged carboxylate ions. The authors have characterized the kinetics of oxidation in terms of bisubstrate Michaelis–Menten rate law. Michaelis–Menten kinetics [217] is typical of enzyme-catalyzed reactions involving a single sub-

FIG. 8. Schematic diagram of proposed mechanism for the CoPcTS-catalyzed oxidation of mercaptans.
strate. The relationship between the rate $v$ and substrate concentration is hyperbolic and can be expressed as follows:

$$
v = \frac{V_{\text{max}}[S]}{K_m + [S]} \quad (14)
$$

where $V_{\text{max}}$ is the limiting rate at high substrate concentration and $K_m$ is the Michaelis constant. This type of kinetics is explained in terms of formation of an addition complex between enzyme and substrate, the complex breaking down in the second step into product with the release of enzyme $E$.

$$
E + S \rightleftharpoons ES \quad (15)
$$

$$
ES \rightarrow E + P \quad (16)
$$

Various factors cause variations in the kinetic law. The variation which is relevant in the present context is the one involving two substrates in an enzyme-catalyzed reaction. One substrate $A$ forms the complex $EA$ with enzyme $E$, which reacts with other substrate $B$ to form a ternary complex $EAB$, which then decomposes into products. This is known as the "ordered ternary complex" mechanism.

Kinetics and reaction mechanism for the oxidation of mercaptans catalyzed by cobalt phthalocyanine tetrasulfonate (CoPcTS) bound to polyamine base were extensively studied by Brouwer et al. [169–176] and by Schutten et al. [178, 179]. The polymeric catalysts showed enzyme-like behavior during oxidation and followed Michaelis–Menten kinetics with respect to substrate concentration and oxygen pressure. In the oxidation of 2-mercaptoethanol with CoPcTS–poly(vinylamine) catalyst [174, 178], the main products formed were the disulfide and hydrogen peroxide. The latter reacted further with the mercaptan, forming another mole of disulfide. The reaction rate was observed to be first-order with respect to the catalyst. The reaction rate showed an optimum around $pH = 8$ [169, 177], caused by the opposing effects on increasing the pH, viz., an increase of mercaptide ion concentration and an increase in ionic strength. The collapse of catalytic activity above the pH optimum was attributed to the loss of polymer charge (deprotonation). Addition of salt caused a severe decrease in the catalytic activity because of a decrease in the local mercaptide anion concentration in the vicinity of the oxidation sites. Addition of radical scavengers also led to a decrease in the reaction rate, indicating that radicals were the reaction intermediates. The high activity of polymeric (CoPcTS–polyamine) catalysts was attributed to the fact that basic polymers inhibited the aggregation of the cobalt complexes [172, 175].

The cobalt phthalocyanine catalyzed oxidation of mercaptans in presence of ionenes was investigated by Brouwer et al. [176, 177] and by Van Welzen et al. [181, 194, 218, 219]. The reaction kinetics followed the two-substrate Michaelis–Menten rate law, in which the mercaptan was one substrate and oxygen the other. The reaction proceeded through the for-
mation of the hydrogen peroxide which subsequently decomposed by further reaction with mercaptan. The effect of various factors such as pH, type of substrate, and type of polymer on the overall reaction rate was essentially similar to the cobalt phthalocyanine bound polyamine base catalyzed reactions. It was suggested [181, 194, 219] that the addition of polyionenes in cobalt phthalocyanine catalyzed oxidation resulted in electrostatic interactions which led to enhanced activities (about 40-fold) in the oxidation of mercaptans. Interestingly, this phenomenon was explained by an enhanced aggregation of the cobalt complex.

VIII. SUMMARY

In the Merox process the catalytic oxidation of mercaptans to disulfides is carried out in alkaline medium in the presence of catalyst consisting mainly of sulfonated derivatives of cobalt phthalocyanine complex. The cobalt phthalocyanine sulfonates and their analogs have been used as catalysts for mercaptan oxidation processes in other countries. Polymeric metal phthalocyanines and cobalt phthalocyanine sulfonates coordinately bound to polymers have been found to be more effective than the conventional cobalt phthalocyanine sulfonate catalysts.

Along with the cobalt phthalocyanine catalyst, various promoters have been used to enhance the catalyst life and activity. A large number of organic compounds have been reported as promoters, of which the most effective are quaternary ammonium hydroxides or chloride, viz., benzyl dimethyl alkyl ammonium hydroxide or chloride.

The mechanism of catalytic oxidation of mercaptans in the presence of cobalt phthalocyanine complexes proceeds via the formation of a ternary complex involving the catalyst, mercaptide anion, and molecular oxygen. The complex then undergoes decomposition through electron transfer resulting in the formation of mercaptide radical and hydrogen peroxide. The mercaptide radicals combine to form disulfide while hydrogen peroxide further oxidizes 2 moles of mercaptans. The oxidation process is similar to the enzyme-catalyzed reactions and follows the Michaelis–Menten rate law.

REFERENCES

133. N. Fukada, Nippon Kagaku Zasshi, 75, 586 (1954); 76, 1378 (1955); 77, 1421 (1956); 79, 396 (1958); 79, 980 (1958).


166. UOP Inc., Belgium 882106, July 1, 1980.


V. I. Shcherbachenko, P. M. Bozhen'kin, and V. A. Tochilov, Neftepererab. Neftekhim. (Moscow), 6, 23 (1979).

A. H. Cook, J. Chem. Soc., 1761 (1938); ibid., 1768 (1938); ibid., 1774 (1938); ibid., 1845 (1938).


H. Kropf, Ann. Chem., 637, 73 (1960); ibid., 93 (1960); ibid., 111 (1960).


N. N. Kundo and N. P. Keyer, Kinetika i Kataliz., 8, 796 (1967); ibid., 1325 (1967).


Xin Qian, Xufan Liu, and Yixun Su, Shiyou Xuebao, Shiyou Jiagong, 2(2), 71 (1986).


