

Catalytic Oxidation

==== **for the Control of** ====
Hazardous Organic Air Pollutants

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Manufacturers of Emission Control Association

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I. Introduction

The Clean Air Act Amendments of 1990 (CAAA) significantly changed the Act adding many new, stricter requirements for previously regulated sources. It also introduced a new title (Title III) to address air toxics or as referred to in the Act, hazardous air pollutants (HAPs). HAP emissions had been previously regulated by the National Emissions Standards for Hazardous Air Pollutants (NESHAPs) Program under Section 112 of the Act. The control requirements were to be based on levels protecting public health with "an ample margin of safety". However, the program was considered largely unsuccessful because of the small number of pollutants regulated and the difficulty in determining the proper control limits to guard against health risks.

In 1990, Congress developed a list of 189 HAPs, of which 154 are volatile organic compounds (VOHAPs), for which new NESHAPs are to be promulgated requiring Maximum Achievable Control Technology (MACT), a technology-based standard in place of a health-based standard. The CAAA also stipulated a strict timeframe for development and approval of the standards. Once the technology based standards are in place, EPA is to determine the residual health risk and make recommendations to Congress by November 15, 1996 as to whether even tighter control requirements are needed and review these every 8 years.

EPA estimates the 189 HAPs are responsible for 1000 to 3000 cancer deaths per year. Some of the 154 VOHAPs are more commonly known substances like benzene, toluene, and formaldehyde. Others are more obscure substances used in or produced as by-products of various industries. All of the VOHAPs can be oxidized catalytically, even those which contain halogens like chlorine, fluorine, and bromine provided the proper catalyst is used.

Widespread use of catalytic oxidation for emission control began in the automotive industry twenty years ago as a result of control requirements in the original Clean Air Act Amendments passed in 1970. Today, over 350 million automobiles are equipped with catalytic converters. However, catalytic oxidation for VOC control for stationary sources began in the 1940's for energy recovery and odor control. Since the early use of catalysts, the technology has evolved considerably in both the automotive and stationary source sectors.

Oxidation catalysts are effectively controlling VOHAPs emissions in industries including bakeries, petrochemical and refining operations, pharmaceutical manufacturing, printing, food processing and a wide range of coating operations among others. Control efficiencies in excess of 98 percent can readily be achieved and some systems have been in use for well over eight years. The systems have been applied to both continuous and batch processes and to small and large operations. And catalyst technology is an available, effective and cost efficient control option for air toxics or VOHAPs.

II. Title III of the Clean Air Act Amendments of 1990

Under Title III, once Congress listed the 189 HAPs to be regulated, EPA was required to identify the various sources which emit HAPs and produce a schedule for promulgation of MACT standards for new and existing major sources. A major source is any source which emits over 10 tons per year (tpy) of a single HAP or 25 tpy of any combination of HAPs. EPA has determined that there are 174 different types of sources of HAP emissions in the U.S. which fall under 16 separate categories (see Table 1). For example, the surface coating category includes automotive coating operations and the coating of metal coil among other industries or operations. Table 2 outlines the 154 VOHAPs included as part of the 189 HAPs listed by Congress.

Table 1: NESHAP Source Categories

Fuel Combustion	Petroleum and Gas Production and Refining	Agricultural Chemical Production	Polymers and Resin Production
Non-Ferrous Metals Processing	Liquid Distribution	Fibers Production Processes	Production of Inorganic Chemicals
Ferrous Metal Processing	Surface Coating Processes	Food and Agricultural Processes	Production of Organic Chemicals
Mineral Products Processing	Waste Treatment and Disposal	Pharmaceutical Production Processes	Miscellaneous Processes

The statutory schedule for promulgation of the NESHAPS is:

- 25 percent of the listed sources by November 1994,
- an additional 25 percent of the listed sources by November 1997,
- all standards promulgated by November 2000.

EPA is further required to promulgate standards for publicly owned treatment facilities by November 1995. EPA also defined eight categories for area sources.

The standards are to achieve the maximum degree of reduction of emissions taking into consideration the cost, non-air quality health and environmental impacts, and energy requirements. In the case of existing major sources, the standards may be less stringent than those for new sources, but must not be less stringent than the average emission limit achieved by the best performing 12 percent of existing sources where there are 30 or more existing sources. Where there are fewer than 30 existing sources, the sources must achieve the average emission limit of the 5 best performing sources.

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Table 2: VOC Hazardous Air Pollutants (VOHAP)

Acetaldehyde	2-Chloroacetophenone	Dimethyl aminoazobenzene	Ethylidene dichloride (1,1-Dichloroethane)	Methyl methacrylate	2,3,7,8-Tetrachlorodibenzo-p-dioxin
Acetamide	Chlorobenzene	3,3-Dimethyl benzidine	Formaldehyde	Methyl tert butyl ether	1,1,2,2-Tetrachloroethane
Acetonitrile	Chlorobenzilate	Dimethyl carbamoyl chloride	Heptachlor	4,4-Methylenedianiline	Naphthalene
Acetophenone	Chloroform	Dimethyl formamide	Hexachlorobenzene	Nitrobenzene	Tetrachloroethylene (Perchloroethylene)
2-Acetylaminofluorene	Chloromethyl methyl ether	1,1-Dimethyl hydrazine	Hexachlorobutadiene	4-Nitrobiphenyl	Toluene
Acrolein	Chloroprene	Dimethyl phthalate	Hexachlorocyclopentadiene	4-Nitrophenol	2,4-Toluene diamine
Acrylamide	Cresols/Cresylic acid (isomers & mixture)	4,6-Dinitro-o-cresol	Hexachloroethane	2-Nitropropane	2,4-Toluene diisocyanate
Acrylic acid	o-Cresol	2,4-Dinitrophenol	Hexamethylene-1,6-diisocyanate	N-Nitroso-N-methylurea	o-Toluidine
Acrylonitrile	m-Cresol	2,4-Dinitrotoluene	Hexane	N-Nitrosodimethylamine	Toxaphene (chlorinated camphene)
Allyl chloride	p-Cresol	1,4-Dioxane (1,4-Diethyleneoxide)	Hydrazine	N-Nitrosomorpholine	1,2,4-Trichlorobenzene
4-Aminobiphenyl	Cumene	1,2-Diphenylhydrazine	Hydroquinone	Pentachlorophenol	1,1,2-Trichloroethane
Aniline	DDE (Dichlorodiphenyl-dichloroethylene)	Epichlorohydrin (1-Chloro-2,3-epoxypropane)	Isophorone	Phenol	Trichloroethylene
o-Anisidine	Diazomethane	1,2-Epoxybutane	Lindane (all isomers)	p-Phenylenediamine	2,4,5-Trichlorophenol
Benzene (including from gasoline)	Dibenzofurans	Ethyl acrylate	Maleic anhydride	Phosgene	2,4,6-Trichlorophenol
Benzidine	1,2-Dibromo-3-chloropropane	Ethyl benzene	Methanol	Phthalic anhydride	Triethylamine
Benzotrithloride	Dibutylphthalate	Ethyl carbamate (Urethane)	Methoxychlor	Polychlorinated biphenyls (Aroclors)	Trifluralin
Benzyl chloride	1,4-Dichlorobenzene(p)	Ethyl chloride (Chloroethane)	Methyl bromide (Bromomethane)	1,3-Propane sultone	2,2,4-Trimethylpentane
Biphenyl	3,3-Dichlorobenzidene	Ethyl chloroform (1,1,1-Trichloroethane)	Methyl chloride (Chloromethane)	beta-Propiolactone	Vinyl acetate
Bis(2-ethylhexyl) phthalate(DEHP)	Dichloroethyl ether (Bis(2-chloroethyl) ether)	Ethyl bromide (Dibromoethane)	Methyl chloroform (1,1,1-Trichloroethane)	Propionaldehyde	Vinyl bromide
Bis(chloromethyl)ether	1,3-Dichloropropene	Ethylene dichloride (1,2-Dichloroethane)	Methyl ethyl ketone (2-Butanone)	Propoxur (Baygon)	Vinyl chloride
Bromoform	Dichlorvos	Ethylene glycol	Methyl hydrazine	Propylene dichloride (1,2-Dichloropropane)	Vinylidene chloride (1,1-Dichloroethylene)
1,3-Butadiene	Diethanolamine	Ethylene imine (Aziridine)	Methyl iodide (Iodomethane)	Propylene oxide	Xylenes (isomers and mixture)
Caprolactam	N,N-Diethyl aniline (N,N-Dimethylaniline)	Ethylene oxide	Methyl isobutyl ketone (Hexone)	1,2-Propylenimine (2-Methyl aziridine)	o-Xylenes
Captan	3,3-Dimethoxybenzidine	Ethylene thiourea	Methyl isocyanate	Styrene	m-Xylenes
Carbaryl				Styrene oxide	p-Xylenes
Carbon disulfide					
Carbon tetrachloride					
Carbonyl sulfide					
Catechol					
Chlordane					
Chloroacetic acid					

To date, under the 1990 CAAA, NESHAP standards have been developed for four sources for which catalytic oxidation can be used to comply. These are the synthetic organic chemical manufacturing, magnetic tape manufacturing industries, epoxy resin and non-nylon polyamides production, and degreasing operations. However in the case of degreasing operations, it is likely that few, if any, of the operations will use add-on controls as means of complying.

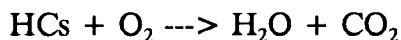
III. Catalyst Technology

a. How it works

Catalytic oxidation is a chemical oxidation process in which hydrocarbons (HCs) are combined with oxygen at specific temperatures to yield carbon dioxide (CO₂) and water.

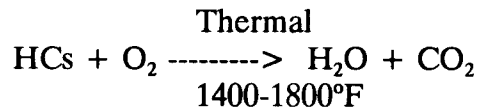
As its name suggests, catalytic oxidation uses a catalyst, a substance that accelerates the rate of a chemical reaction without itself being consumed.

The most widely used method of reducing VOHAPs from industrial exhausts is incineration. In general, the reaction takes the form:

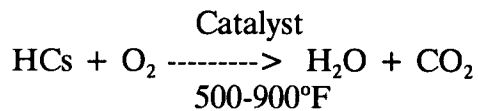


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Either thermal or catalytic methods may be used to achieve this reaction. At elevated temperatures, the molecules of hydrocarbon and oxygen have sufficient energy to react directly with each other to form carbon dioxide:



Catalysts lower the reaction's activation energy, the energy necessary for the molecules to react. With a catalyst present, the same reaction occurs, but at a lower temperature resulting in lower operating and/or capital costs.

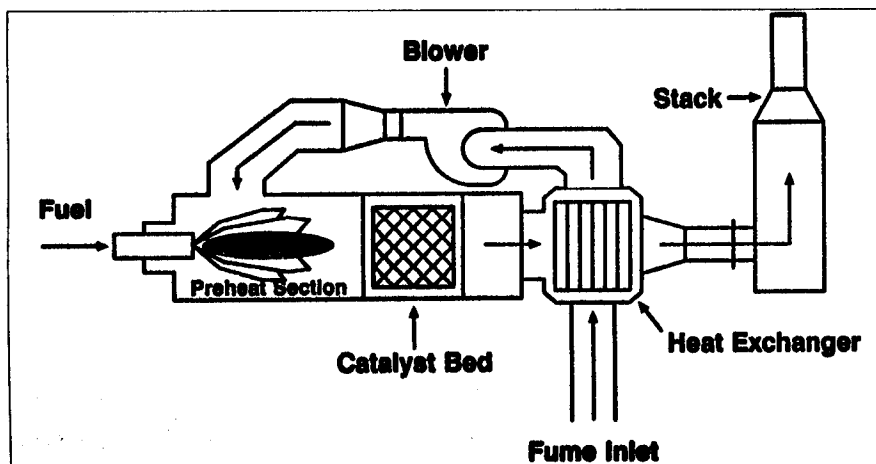


Many chemical elements exhibit catalytic activity. However certain precious metals and rare metal oxides -- especially platinum, palladium, rhodium and manganese dioxide -- have application in gaseous emission control. Each precious metal or metal oxide has unique characteristics, and the correct metal or combination of metals must be selected for each VOHAP control application.

The selected catalyst is placed on a carrier or mixed with a carrier to produce a wide dispersion of the catalytically active metal and create a large surface area. The carrier is a mechanical support structure, which may be in the form of beads, woven mesh, screens, or ceramic and metal honeycombs.

In a typical catalytic control system (Figure 1), process gas containing VOHAPs passes through the catalyst element after first being heated in a preheat chamber where its temperature is raised above the catalytic ignition temperature (typically 400°F to 500°F). Oxidation of VOHAPs occurs on the surface of the catalyst; heat is released as the VOHAPs are converted to CO₂ and H₂O. The purified gas stream is vented through a flue or stack but may first pass through a heat exchanger, to recapture heat which can then be used to reduce the fuel required to heat the preheat chamber. Adiabatic temperature increases over a catalyst bed are given in Table 3 for selected VOCs and VOHAPs.

Figure 1: Typical Catalytic Oxidation System



**Table 3: Adiabatic Temperature Rise
(per 100 ppm)**

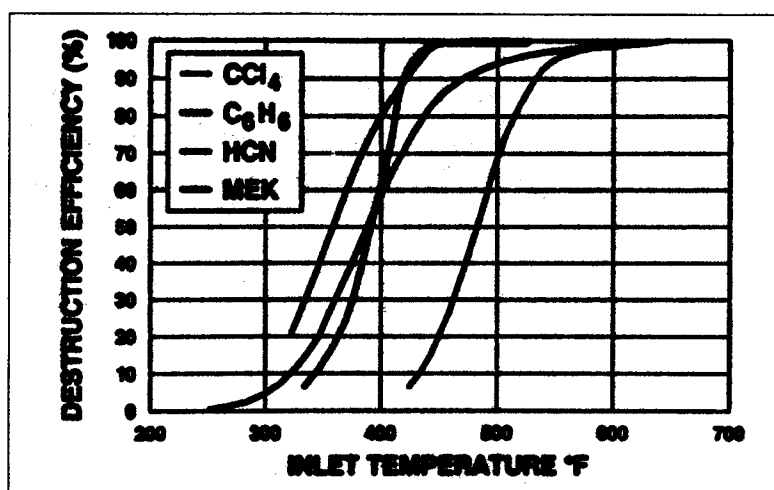
Methanol	3-4 °F
Ethanol	7-8 °F
Propane, Propylene	11-12 °F
Toluene, Xylene	23-26 °F
Octane, Hexane	23-30 °F

b. Control Capabilities

The level of control efficiency achievable by catalytic oxidation is designed into a catalytic control system; it is a design parameter. Control efficiency is determined by plant process characteristics such as the type and concentration of VOHAPs emitted, flow rate, process fluctuations that may occur in flow rate, pressure drop, temperature, concentrations of other materials in the process stream, and the governing permit regulation (such as mass emission limit). Control efficiencies yielding 99 percent VOHAP destruction have been designed, achieved and maintained for many years in commercial installations. For example, in the wood products industry, catalysts have been used to abate residual formaldehyde, one of the Title III VOHAPs, discharged during wood processing. Recently, customers have measured performance in excess of 99 percent destruction in this application. In fact, destruction efficiencies as high as 99.9 percent can be achieved for many of the VOHAPs. For example, the destruction of ethylene oxide with MnO_2 and the destruction of acetaldehyde with Pt.

Figure 2 shows typical destruction efficiencies as a function of temperature for four Title III VOHAPs: carbon tetrachloride (CCl_4), benzene (C_6H_6), methyl ethyl ketone (MEK), and hydrogen cyanide (HCN). As shown, the highest temperature required for a greater than 99 percent destruction efficiency is 610 °F for CCl_4 .

Figure 2: Destruction Efficiencies for some VOHAPs



c. Advantages of Catalyst Technology

In comparing catalytic oxidation to thermal destruction of the four VOHAPs, some inherent advantages of catalytic oxidation become apparent. Using HCN, the most difficult of the four VOHAPs to destroy thermally, as an example, a thermal incinerator would be required to operate at temperatures of 1800 °F with a retention time of 1.5 seconds to achieve in excess of 99 percent destruction. This compares to a catalytic system which is required to operate at 480 °F with a retention time 0.24 seconds to achieve the same destruction efficiency. Hence, the thermal incinerator would require a reactor more than six times the size of that of the catalytic system. The higher temperatures required by thermal incinerators require more robust materials of construction and consume more energy than catalytic systems. Another advantage of catalytic systems is that there is minimal NO_x production because of their low operating temperatures and any CO generated in the operation of the burner is oxidized to CO_2 resulting in no net increase.

d. Operating Condition Considerations

In employing catalytic oxidation in controlling VOHAP emissions, there are, however, operating conditions which can reduce catalytic activity. Catalytic deactivation may result from (1) masking, (2) chemical poisoning, or (3) thermal sintering. All three can take place slowly; the overall process is often called "aging". Numerous VOHAP catalytic applications have operated for ten years and more without measurable loss of catalyst performance.

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Some installations, however, do experience performance loss over time. In most of these cases, the reduced performance results from the catalyst being masked by contaminants in the exhaust. Catalyst manufacturers can test such a catalyst, taking a sample from the lower-performing unit to determine the cause of the activity loss and the best method of regeneration. Cleaning procedures can remove contaminants from the catalyst, usually restoring catalytic activity to close to the original level.

Chemical poisoning of a catalyst is often thought of as being permanent. However, in many instances, the effects of it can be reversed with special procedures. Poisoning is less of a concern with today's high technology catalysts, many of which are formulated to be poison resistant.

Thermal sintering of the catalyst is not reversible because it causes a collapse of the washcoat. However, this type of change would be the result of system upset or misoperation, and steps can be taken by the source operator to guard against this type of occurrence.

IV. Catalytic Oxidation Applications for VOHAPs Control:

Catalytic oxidation has been used for over 17 years for VOHAP emissions control. Today, most of the world's catalytic oxidizers are used in the U.S., Germany, and Japan, for a wide range of applications including automotive paint baking, can coating, coil coating, printing operations, commercial baking, chemical manufacturing, and more. The chemical industry was the first to utilize catalytic oxidation extensively for emission control, with units capable of treating up to 100,000 scfm (standard cubic feet per minute) of exhaust gas containing VOHAPs. Larger units (500,000 scfm) have been used in paint bake applications, particularly for the automobile and aerospace industries.

Several industries use much smaller units. In the can coating industry, more than twenty five units are in use, ranging in capacity from 5,000 to 20,000 scfm. The food industry uses units in this size range to treat odor; some ten to fifteen units also in this size range are used in the fabric coating industry. Recently, about 1200 catalytic oxidizers have been installed in the U.S., for use in the printing industry. By 1995, over 3,000 catalytic oxidizers had been installed worldwide. Table 4 outlines some of the catalytic oxidation experience obtained for VOHAP emissions control. Also shown is the destructive efficiency the systems have been designed to achieve. In many instances, catalytic oxidation can be used to achieve much higher destruction efficiencies than shown in the table. An additional advantage of catalytic controls is that their destruction efficiency can be directly monitored, unlike other technologies such as flares.

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Table 4: Typical Catalytic Oxidizer Applications

Application	Typical Organic Compounds and Solvents	Years in Service	Destruction Efficiency
Can Coating	MIBK , Mineral Spirits Iso-Phorone , DIBK Butyl Cellosolve	5	95%
		5	95%
		5	95%
		12	95%
		8	90%
Metal Coating	MEK , MIBK , Toluene i-Butanol	4	95%
		8	90%
Auto Paint Bake	MEK , Toluene , Xylene	4	95%
		4	95%
		3	95%
		10	95%
Glove Manufacture	Formaldehyde , Phenolics	3	90%
Phthalic Anhydride	PA , MA , S	12	95%
Flexible Packaging	Acetates , Alcohols , Ketones	5	95%
Vinyl Coating	Ketones , Aromatics	5	95%
Phenol Manufacture	Cumene , Acetone	4	97%
Film Coating	Ketones , Acids	7	95%
Formaldehyde Manufacture	Methyl Ether, CO, Methanol, Formaldehyde	5	98%
Septic Packaging (Edible) instance	Alcohols , Acetates	7	97%

Note: VOHAPS highlighted in bold.

Not all considerations will argue, of course, in favor of catalytic oxidation; it is not an all-purpose solution. But particularly where effective, reliable removal of VOHAPs, ease of operation, long-term performance and low operating and maintenance costs are key considerations when evaluating and specifying VOHAP control technologies, we believe that catalytic controls will often be shown to provide the most control solution.

As evidenced by the table, catalytic oxidation has been employed in a variety of industries to control a broad range of VOHAP emissions. In fact there are over 3,000

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systems worldwide controlling VOHAP emissions with destruction efficiencies exceeding 99 percent in some instances.

To date, four NESHAPs that could use catalytic oxidation as an appropriate control strategy have been finalized:

- synthetic organic chemical manufacturing industry (SOCMI),
- magnetic tape manufacturing,
- degreasing operations,
- and epoxy resin and non-nylon polyamides production.

Of these, it is likely that catalytic oxidation will be used as a control strategy in three of these industries. In all likelihood, degreasing operations will rely on procedural and operational changes in order to comply with the rule. The MACT standard for SOCMI has been promulgated as a 98 percent reduction of VOC or a reduction to less than 20 ppmv. Catalytic oxidation readily achieves either of these criteria. On the other hand, the MACT standard for magnetic tape manufacturing has been promulgated as a 95 percent reduction or an outlet concentration of less than 20 ppmv. Again, catalytic oxidation can achieve these requirements. In fact, the technology can exceed the promulgated standard. As with SOCMI, greater than 98 percent VOC reductions can be achieved.

EPA has proposed a number of additional NESHAPs (See Table 5) where catalytic oxidation catalyst could be used to meet or exceed the proposed levels of control.

Table 5: Additional Proposed NESHAPs Where Catalytic Oxidation Can Be Used

Proposed Rule	Expected Final Date
Petroleum Refineries	June 1995
Aerospace Industry	July 1995
Pulp and Paper Industry	September 1995
Wood Furniture Manufacturing	November 1995
Off-Site Waste and Recovery Operations	November 1995
Group IV Polymer and Resin Production	March 1996

7. Conclusion

Catalytic oxidation has been used to control VOC and VOHAP emissions for over forty years. Destruction efficiencies in excess of 99 percent can be achieved for many of the VOHAP emissions regulated under Title III of the 1990 CAAA. Catalytic oxidation can be used in many instances to emission levels lower than the proposed MACT standard.