Platinum Oxidation Catalysts in the Control of Air Pollution

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Catalytic combustion as a means of controlling or eliminating unpleasant fumes from industrial processes has made considerable progress, and many air pollution problems are now being solved in this way. This article demonstrates the versatility of the method and gives some examples of the success achieved when the control equipment is properly engineered.

Catalytic oxidation is a combustion process for controlling odours or visible fumes exhausted from industrial processes. It offers certain advantages over other methods of combustion in terms of efficiency and of the temperatures required for oxidising the contaminants.

Generally speaking, catalytic installations are usually associated with waste gases which are relatively free from so-called catalyst poisons such as metallic oxides and other non-combustible contaminants. In applications to industrial drying ovens for paint baking, wire coating, investment casting, and others, the effluents are found to be composed essentially of a mixture of air and pure hydrocarbons or other gases which can be oxidised completely to CO_2 and H_2O. It would be erroneous, however, to believe that catalytic oxidation must be limited to these simple and ideal applications. The problem of catalyst contamination can, in many cases, be resolved by engineering and the use of appropriate catalytic elements. This article discusses a number of successful cases where catalysts are being used in the presence of materials generally believed to be deterrents to catalytic oxidation.

Principle of Catalytic Oxidation

In order to understand the logic behind the design and operating conditions, it is necessary to analyse briefly the phenomenon of catalytic oxidation. It is generally accepted that the combination of molecules of the combustible gases and oxygen takes place at the surface of the catalyst. The rate at which this phenomenon occurs determines the activity of the catalyst. The physical and chemical characteristics of catalytic surfaces have an important bearing on the relative activity or rate of reaction of different catalysts. Recognising this basic fundamental, it is obvious that to realise a successful catalytic oxidation reaction, the following factors must be considered:

(1) Precautions must be taken to minimise deposits on the catalytic surface, or clogging, in order to maintain contact with the molecules of combustible gases and the oxygen.

(2) The catalytic agent must be extremely active and must be applied uniformly to the carrier. A deposit or coating is less apt to hinder the reaction on a very active catalyst surface than on one which is less active.

(3) The catalytic element must be designed in such a way as to permit an even and equal flow over the catalyst surface and through the bed. If there is an entrainment present in the stream, the chance of clogging and contamination is reduced by

maintaining equal velocity and even distribution of the gas flow. This also minimises the problem of erosion of the catalyst surface, since this condition can occur when the catalyst surface is exposed to an excessive gas velocity and the gas contains abrasive particles.

From the above, it is clear that the role of the catalyst itself in resisting contamination or poisoning cannot be over-emphasised. A very active and stable catalyst is able to withstand the presence of contaminating agents far more efficiently than one which is less active. By experimentation and in commercial installations it has been shown that one catalyst will function satisfactorily for several thousand hours, whereas another form of catalyst will be poisoned in a matter of a few hours under the same conditions. It is extraordinary to note that the difference in the behaviour of catalysts can be so great when the catalysts are composed of the same basic elements but of different preparation or configuration.

The catalytic element used on the installation described here is known commercially as the Oxycat. In the composition and design of this element detailed consideration has been given in the preparation of this catalyst to obtain the desired characteristics already described.

Fig. 1 shows a cross section of one of these elements. It consists of two porcelain end plates holding in place 71 porcelain rods evenly staggered in the unit. The unit measures $5\frac{1}{2}$ inches long, $3\frac{3}{16}$ inches high, and 3 inches wide. The rods are spaced at approxi-

mately $\frac{1}{4}$ inch intervals. This permits passage of solid particles up to $\frac{3}{32}$ inch through the bed without clogging. The rods are also streamlined in the form of neutral aerofoils to reduce turbulence, thereby minimising back pressure and assuring a maximum surface contact with the gas stream. An equally important factor is the theoretical behaviour of aerosols and other small particles in passing over an aerofoil section. Whereas such particles would normally impinge on the surface, due to the tear-drop design they flow in a pattern similar to the gas molecules and pass over the surface without impinging.

The catalytic agent of the Oxycat is a combination of platinum and alumina. The proportion of platinum and alumina used is a result of an extensive study and research programme. The porcelain used in the carrier is a high-grade spark-plug type, selected because of its strength, chemical inertness and resistance to high temperatures. The design and composition of the Oxycat permits operating temperatures as high as 1800°F which, in itself, is a feature that has greatly extended the possible fields of application.
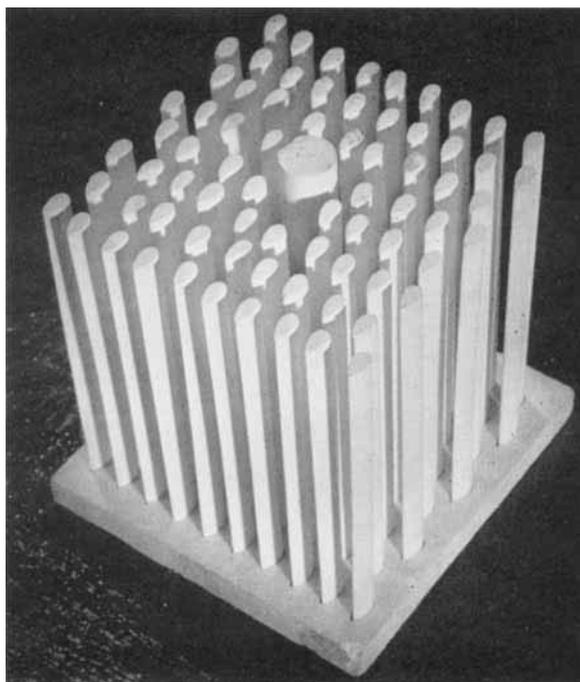

Fig. 1 A single Oxycat unit of aerofoil section porcelain rods carrying a platinum-on-alumina catalyst

Fig. 2 Units can be stacked horizontally and vertically to form catalytic beds of any size to meet the requirements of a plant design

The configuration and dimensions of the Oxycat enable the stacking of these units side by side and in layers to form catalytic beds of any size, as shown in Fig. 2.

The application of this principle to four industrial processes, each quite different in the problems it presented, is described in the remainder of this article.

Curing Operations on a Resinous Binder

The first installation under consideration is one in which a resinous binder is applied to rock wool or Fibreglass. The material is then introduced into an oven where the binder is cured. In this curing operation resinous materials are emitted which create an air pollution problem. While oxidation of these combustible resinous contaminants can readily be accomplished by catalytic oxidation, entrained in the exhaust stream there are threads of the rock wool or Fibreglass which can cause plugging of the oxidation catalyst. A flow diagram of this installation is shown in Fig. 3.

After passage through the exhaust fan, the effluent is heated by means of the pre-heat burner and passed through the Oxycat bed. Between the pre-heat burner and the catalyst bed two stainless steel screens are installed in series to take out the major part of the entrained threads. These screens have been constructed so that they are easily removed for cleaning. They are located after the pre-heat burner since, at this point, the combustible contaminants are in a vapour state and readily pass through the screens; the deposit is therefore accumulated on the screens as dry Fibreglass material which is easily removed. A certain percentage of the threads does pass through these screens, but the design of the Oxycat allows passage of most of the remainder of the material. In actual installations it has been found that there may be sufficient accumulation of fibres on the catalyst to necessitate cleaning operations every two or three months. Other forms of catalyst would become ineffective in a matter of days. The elements here can, however, be cleaned

without being removed by blasting compressed air through the bed. For this reason it is desirable to design the catalyst chamber so that the catalyst bed is readily accessible either for removal or cleaning.

Catalytic Cracking of Petroleum

A second application is in connection with catalytic cracking plants. Catalytic cracking is a process which has been widely adopted by the oil industry to make high octane gasoline. The gases from the regenerator, which are the waste gases, are rich in combustibles containing anywhere from 3 to 8 per cent of carbon monoxide, plus some hydrocarbons. At first glance, this seems like an ideal application for catalytic oxidation. However, the gases, in addition to the combustibles, contain varying amounts of cracking catalyst dust or beads which are composed essentially of special types of alumina and silica.

Cracking units are usually equipped with precipitators or cyclones which remove the major portion of the cracking catalyst carry-over before introducing the stream to an Oxycat system. Even with the most effective separators, a certain quantity of fines pass through the Oxycat bed. The physical characteristics of the Oxycat permit passage of the fines without adherence to the surface, but the extremely abrasive nature of these fines demands careful precautionary measures against erosion of the catalyst surface. The design of the catalyst carrier makes possible an even flow through the bed and, consequently, the velocity of the gases can be maintained comparatively constant throughout the various sections of the catalytic mass. Erosion is, therefore, solved by engineering the installation to realise an even and low velocity of the gases over the catalytic surface. These installations are designed for a maximum rate of flow of 25 feet per second.

Since the gases from the regenerator are deficient in oxygen, air must be added to supply the oxygen for complete combustion of the carbon monoxide and hydrocarbons. After mixing, the gas and air mixture may
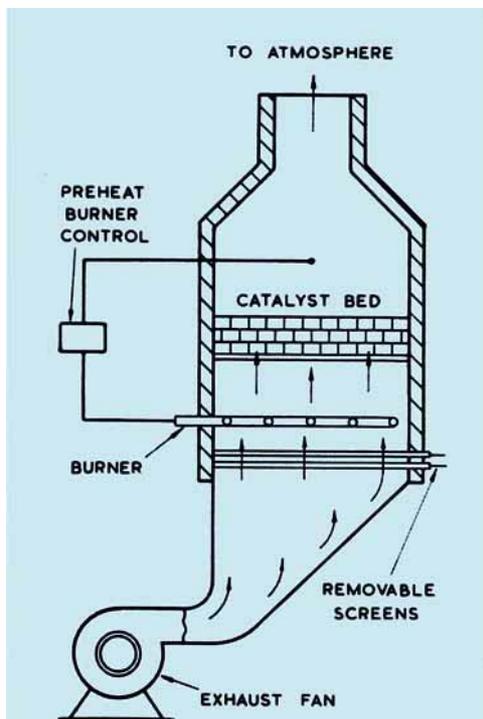

Fig. 3 An installation for the catalytic oxidation of resinous contaminants. Threads of Fibreglass carried by the exhaust stream are first removed by the screens

necessitate pre-heating to reach a minimum temperature of 650°F which is the temperature required in this particular application for the catalytic reaction to occur. The pre-heating is normally accomplished by line burners using refinery gas or oil as fuel. Following mixing and pre-heating, the gas stream enters the catalyst chamber through an inlet designed to disperse the stream uniformly throughout the bed. The catalytic oxidation reaction results in a temperature rise of 600 to 900°F, bringing the final temperature of the gas stream emerging from the catalyst to 1300 to 1600°F. This gas is then introduced into a waste heat boiler to generate steam required to operate the catalytic cracking unit or other equipment. The heat that can be generated from oxidising the waste gases from some of the larger units is sufficient

to raise as much as 300,000 lb. of steam per hour. The pay-off in terms of fuel recovery is extremely attractive—often less than two years, depending on local fuel costs. There are several installations of this type in use, one of them having been on stream for over two years without any evidence of erosion or reduction in catalyst activity. While these installations are primarily for heat recovery, they also eliminate the objectionable plume which is usually associated with cat crackers.

Manufacture of Carbon Black

The third example under discussion is one which is applied to carbon black manufacturing processes. These processes have tail gases which contain large quantities of combustibles. Entrained carbon black creates a considerable air pollution problem which may be the motivating force for such an installation. There again the economics are so attractive that these installations can also be justified for heat recovery alone. The heat generated is used to produce steam and can also be used to pre-heat the fuel from which the carbon black is made. Fig. 4 shows the flow in such a system.

As the gases in this operation are deficient in oxygen, air is added to supply the oxygen required for catalysis. It is necessary to preheat this mixture since the waste gas is received at a temperature of approximately 300°F. The addition of air, of course, reduces this temperature somewhat. Experience has shown that a temperature of approximately 600°F entering the Oxycat bed is required to maintain catalytic activity of these gases with the entrained carbon black. This is accomplished initially by means of the pre-heat burner installed on the upstream side of the Oxycat bed. After pre-heating to 600°F, the combustible vapours are oxidised within the Oxycats and a temperature of approximately 1600°F is realised emerging from the catalyst.

Some oxidation of the particulate carbon black is also achieved. However, there is no evidence to indicate that this is a catalytic

reaction. It is merely the oxidation of carbon black due to its contact with a hot surface, in this case, the Oxycat. While virtually complete elimination of the combustible vapours is achieved in the catalyst, only about 40 per cent oxidation of the carbon black is effected. To increase the efficiency of carbon black oxidation, checker-brick is provided following the catalyst bed which, of course, assumes the
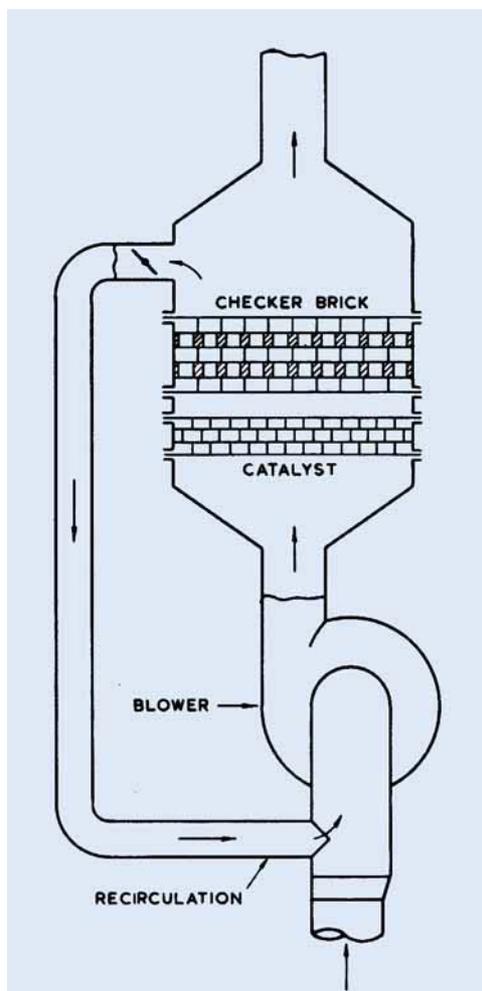

Fig. 4 A system designed for treating the tail gases from carbon black manufacture. Additional air is supplied to provide oxygen for the catalytic reaction and the air/gas mixture is pre-heated. The checker-brickwork is provided to complete the oxidation of the carbon black particles

stream temperature of approximately 1600°F and presents a hot surface to complete the oxidation of carbon black. Continuous operation without the necessity of adding supplementary heat to increase the inlet temperature from 300 to 600°F can be achieved by recirculating a portion of the gases after catalysis and combining them with the tail gas/air mixture.

This is another case where the catalyst bed must be capable of long operation under high temperatures and other severe operating conditions. A very active catalyst is necessary to obtain an homogeneous catalyst skin temperature sufficiently high to burn almost instantaneously the carbon which deposits on the surface. A slow rate of burning would result in a build-up of carbon which would keep the molecules of gas from entering into contact with the catalyst surface and eventually kill the reaction.

A Phthalic Anhydride Process

The fourth example is one in which the tail gases from a phthalic anhydride process are catalytically oxidised to eliminate an air pollution problem.

In this case the exhaust gases are at a low temperature and contain relatively small amounts of combustible materials which are nevertheless obnoxious. The carbon monoxide present in the stream represents the largest quantity of combustibles. Carbon monoxide in itself does not appreciably add to the air pollution problem; the main offenders are the other contaminants, phthalic anhydride, maleic anhydride, naphtha quinone, and formaldehyde. The formaldehyde generally is the one that is most objectionable to the average person. In this type of installation oxidation is achieved at a catalyst inlet temperature of approximately 650°F, the outlet from the catalyst being at approximately 750°F. The difference is achieved by oxidation of the combustibles. The carbon monoxide is a material contributor to this 100°F increase. A flow diagram of such an installation is shown in Fig. 5.
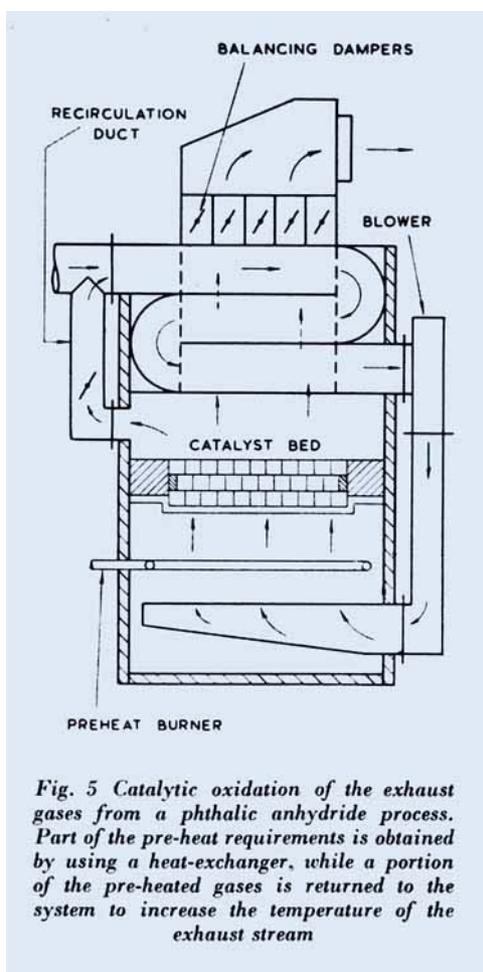

Fig. 5 *Catalytic oxidation of the exhaust gases from a phthalic anhydride process. Part of the pre-heat requirements is obtained by using a heat-exchanger, while a portion of the pre-heated gases is returned to the system to increase the temperature of the exhaust stream*

In this system a portion of the pre-heat requirements for the catalyst bed is obtained by the use of a heat exchanger. Another interesting engineering feature is the provision for returning a portion of the pre-heated gases back to the system to increase the temperature of the waste gas to a minimum of 225°F. This is necessary to prevent corrosion of the heat exchange surface due to the acids present in the stream. Here again the catalyst must be designed to withstand long operation without a reduction in catalyst activity. The gases usually contain aerosols as well as some iron oxide and sulphates resulting from the highly corrosive effect of the gases on the system. Unless the catalyst has a very high activity level, these contaminants are sufficient

to reduce the efficiency of the system in a very short time. Oxycats have functioned on a typical phthalic anhydride waste gas stream for two years without appreciable reduction of activity or necessity of cleaning even though inspection of the bed after 18 months showed evidence of the penetration of the aerosols and a deposit of iron sulphate.

Engineering for Complex Process Streams

For this type of process and for most applications involving complex gas streams, the catalyst should not be exposed to the stream below operating temperature. The catalyst surface can be damaged by an excess of condensable deposits, such as resins and other carbonaceous materials. This condition is easily avoided by using a damper arrangement and by-passing the catalyst until the system has reached a minimum temperature.

The use of oxidation catalysts for air purification is not new, but much progress has been made in applying the principle for industrial use. New avenues are constantly being explored and, as demonstrated, many industrial odour problems caused by organic or combustible contaminants are being solved catalytically, regardless of the complexity of the process streams, by proper engineering and application.

Before these new techniques were fully developed such installations were often considered quite impractical due to excessive costs as a result of frequent catalyst replacement and other operating difficulties. Air pollution control equipment can only be successful if designed and built to operate with the same efficiency and reliability as other plant equipment.

Immersion Thermocouple Practice in the USA
BENEFITS OF TAPPING TEMPERATURE CONTROL IN OPEN-HEARTH FURNACES

The metallurgical and economic advantages to be obtained by using the platinum : rhodium-platinum immersion thermocouples were emphasised in the course of a paper on "Basic Open-hearth Steelmaking in the USA" presented during the meeting of the Iron and Steel Institute held in June in Belgium and Luxembourg (*J. Iron Steel Inst.*, 1958, **189**, (July), 205–216).

The authors, Dr. M. W. Lightner and Dr. D. L. McBride, both of the United States Steel Corporation, recall that for some time most steel plants confined their use of the immersion couple to recording bath temperatures just before tapping or furnace deoxidation. It was soon recognised, however, that the thermocouple could be a valuable tool for controlling bath temperatures within a prescribed range so that furnace banks and bottoms would not be damaged by getting heats too hot, while excessive ladle skulls could be minimised by avoiding cold heats.

Control charts were therefore established showing the relationship between bath temperature and carbon content which would permit rapid ore feeding without chilling the bath.

Throughout the plants of the United States Steel Corporation every effort is now made to tap all heats within $\pm 15°F$ ($\pm 9°C$) of the prescribed temperature. It is found that, with proper attention, all plants can tap at least 80 per cent of their heats within specified temperature range, some plants consistently achieving 90 per cent compliance.

The excellent control of tapping temperatures has been accompanied by a substantial improvement in pouring practice, while other benefits obtained include a 21 per cent decrease in heats downgraded on account of skulls and a 22 per cent reduction in stool consumption. These improvements in quality have been achieved concurrently with a 7.5 per cent decrease in heat time.