

## **Technical Information**

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### **Activity depreciation of KATEC-Metallic-Catalysts**

The Causes and Remedies thereof:

Loss of catalytic activity may be seen through a decrease in combustion performance. Special types of deactivation can lead to the complete ineffectiveness of the catalyst.

Loss of catalytic activity through such causes must not be confused with the destruction of catalysts from excessively high temperatures or other improper uses, but rather more, loss of catalytic activity caused by external influences.

Deactivation may occur if the following components are present in the exhaust gas stream:

- Aerosols/Condensate
- Dust particles (metal oxides, silicates)
- Carbon
- Permanent surface poisons
- Temporary surface poisons

The restoration of catalytic activity after a deactivation has taken place is relatively simple by washing the catalyst, increasing the temperature of the exhaust gas stream etc. In the case of a permanent catalyst poisoning a reactivation by totally renewing the catalyst surface is necessary.

#### **1. Mechanical Deposits on the Catalyst Surface Area**

Such deposits are typically inert dust deposits of aerosols/condensates or a deposition of metal oxides originating from metallic organic vapours on the external surface of the catalyst. The covered surface area of the catalyst is catalytic ineffective. Because of the raising deposition of such materials the catalyst is losing its activity. This causes in a continuous decrease in the combustion efficiency for hydrocarbons.

##### **Dust**

In most catalytic exhaust gas treatment applications dust particles in exhaust gases are occurring either not at all or only in small quantities so that it does not represent a problem.

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For example a high standard of cleanliness and purity for drying air is maintained in the lacquer and varnished coating industry (wire coating, etc.) due to the workpieces to be coated which means the problems with dust are not met.

Exhaust gases from other industrial processes may contain relatively high concentrations of dust particles. In such cases a dust separation must be carried out before the catalytic exhaust gas treatment otherwise the catalyst will rapidly become covered and regeneration of the catalyst has to be carried out after a too short time interval.

If dust removal by separation is impracticable then in such cases one should, if possible, consider implementing a thermal incineration system in place of a catalytic exhaust gas treatment process.

Experience shows that dust concentrations in exhaust gases of several  $\text{mg/nm}^3$  ( $\text{Nm}^3 = \text{STD cubic meters}$ ) necessitate the need for excessive catalyst regeneration. As already mentioned in such cases, dust removal by separation should be carried out prior to the regeneration process sequence. The size and chemical properties of the dust influence the extent of the dust problem. Coarse and inert dust particles (oxides, silicates, etc.) are less problematic than fine and/or corrosive dust particles (salts etc.)

### **Carbon**

Catalysts can be covered with carbon. The formation of carbon deposits on burners or also in catalysts can be caused by incomplete combustion or more accurately thermal cracking of hydrocarbons in the presence of insufficient oxygen in the exhaust gas.

Carbon deposits should be removed by washing and not by stripping at increased catalyst temperature. The stripping of carbon could produce such high exothermal reaction temperatures that the active components of the catalyst could be damaged or even totally destroyed.

### **Metal Oxide**

Metal oxides may be deposited on the external surface area of the catalyst if e. g. during lacquer coating applications with solvents in which metal organic components, which form part of the bonding agent, are set free. As an example Butyltitanate may be mentioned, which is added to lacquers to act as a hardening accelerating agent and

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which may possibly in some cases be found as trace quantities in the exhaust gas, if the evaporation rate of the solvent is too rapid. On contact with the catalyst the organic portion of this compound oxidizes whereby the metal in the form of its oxide ( $\text{TiO}_2$ ) is left coating the external surface area of the catalyst.

This precipitation of metal oxide out of the gas phase may be compared with the precipitation of liquid droplets out of the liquid vapour phase.

Generally the precipitation is laying relatively weak on the catalyst surface and can be removed for the most part by light tapping.

Usually mechanical deposits (with the exception of organic condensates) may be removed from the catalyst external surface area by washing with water. By this means the covering coating will be removed and the surface area will be free again. The catalyst reaches its original level of activity once again.

In difficult cases whereby the oxide coating has been burnt into the external surface area of the catalyst due to the delay of washing in time, washing with a dilute acid solution must be considered (in particular dilute nitric acid, axalic acid and similar).

For practical purpose acid washing should be carried out by the catalyst manufacturer or consumer after consultation and receipt of detailed instructions from the same. (c. f. Technical Information No. 10)

The method of catalyst washing is described in the "Technical Information No. 9" under the title -Instructions for water washings of KATEC Allmetal Catalysts-.

In the case of mechanical coatings with metal oxides, which do normally not occur, washing at regular intervals – approximately every three months – is necessary. e. g. There is no instance known when using a catalytic process for exhaust gas cleanup in the lacquer and varnish coating industry (electrical insulating wire, plating etc.) where washing had to be carried out at shorter intervals. Should be the washing necessary in shorter intervals, then tests should be carried out to determine whether the volatility of the metal organic components in question can be reduced by varying the drying relationships.

If necessary the lacquer manufacturer can consider the replacement of the metal organic additive in the lacquer in return for a less volatile banding agent.

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### **Condensates**

Predominantly polymeric organic combinations with high boiling points can be present in the form of aerosols at low exhaust gas temperatures.

Aerosoles require higher incineration temperatures. If one does not consider this fact then the precipitation of condensates onto the external surface area of the catalyst may occur.

Even if the catalyst in its cold state is carelessly subjected to exhaust gas, condensation occurs on the external surface area of the catalyst.

All condensate precipitations are leading to mechanical coating of the surface area and at the same time to a reduction in the effectiveness of the catalyst in terms of incineration of hydrocarbons.

Condensate precipitation can be evaporated (without removing the catalyst element from the exhaust gas duct) by slowly increasing of the exhaust gas temperature.

This procedure however is not recommendable due to the possibility of damage of the catalyst external surface area through burn-up.

On the assumption that there are still some free active cells of the catalyst it can occur a slow increase of the burning zone through the temperature increase of the exhaust gas. This process can occur with slow evaporating and incineration of the condensates without any detrimental effect on the catalyst activity.

However a rapid burn-up of the condensates is possible. As a direct result of the accompanying higher temperatures damages to the catalyst material are possible so that a premature reactivation of the catalyst becomes necessary.

In exceptionally serious situations even melting can occur which leads to holes being burnt in the support structure of the catalyst. These catalysts must then be completely replaced.

If complete coating with condensate film occurs the catalyst becomes totally ineffective. This condition can be suitably reversed just like any other form of condensate precipitation by removing the catalyst element and allowing the condensate to slowly evaporate over a hot air stream without burn-up occurring. These condensate vapours must of course be extracted from the work shop in questions by means of an appropriate

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ventilation system. Removal of condensate from catalysts is best performed at the catalyst manufacturers plant. On purchase of an appropriate hot air box, the consumer can carry out this procedure by taking necessary precautions.

### **2. Permanent Catalyst Poisoning**

There are a number of elements respectively their compounds which can act as potentially permanent contact poisons. The process of permanent catalyst poisoning may be seen as poison components reacting with the active catalyst metal to form compounds which render the metal as such, catalytically ineffective. It is only a question of concentration of such contact poisons in the exhaust gas and time until the external surface area of the catalyst is transformed to an extent where the profits gained through incineration of hydrocarbons is no longer acceptable. It may be said that the irreversible transformation of the catalysts external surface represents an additive effect.

Typical permanent catalyst poisons are phosphor compounds (e. g. as phosphoric acid or its ester), silicon compounds (e. g. as silicon), as well as the elements zinc, tin lead etc. especially in the form of metallic vapours. However also a whole series of certain inorganic compounds of these elements as well as mercury and arsenic can represent potential contact poisons. As measures for the repair of a permanently deactivated catalyst element only a reactivation should be considered.

Should the situation of a permanent deactivation of the catalyst arise, it should be investigated in liaison with the lacquer manufacturers if it is not possible to replace the lacquer additive responsible for the contact poison in question with a non-deactivating additive. If this is impossible it should be considered to replace the catalytic system with a thermal incineration system.

### **Temporary Catalyst Poisoning**

So called inhibitors or activity reducing agent can lead to a partial or if such agents are present in high concentrations in the exhaust gas to a total stoppage of catalyst activity. This type of deactivation is a direct consequence of preferred adsorption of inhibitors on the active surface area of the catalyst which blocks the desired adsorption of oxygen on the surface area necessary for the catalytic oxidation of hydrocarbons. The higher the concentration of these inhibitors the more critically their effect on the catalytic reaction and consequently on the transformation during the incineration of the hydrocarbons.

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As soon as the gas stream is free of inhibitors the activity of the catalyst increases once more and the transformation during the incineration returns to normal. This is the main difference to a permanent deactivation of a catalyst. In the case of permanent poisoning, a reactivation of the catalyst is most definitely necessary in order to restore the effectiveness.

In the case of temporary poisoning on the other hand only the removal of the activity reducing agent from the exhaust gas is necessary to reinstate catalyst its activity again.

Amongst the inhibitors belong halogens, chlorine, fluor bromide, iodine and some of their compounds, sulphur dioxide, hydrogen sulphide, etc. There exists a certain compatibility between the catalyst and halogens, sulphur dioxide and similar.

The maximum permissible concentration for halogens is approximately 100 mg/Nm<sup>3</sup> (Nm<sup>3</sup> = STD cubic meter) and for sulphur dioxide SO<sub>2</sub> approximately 400 mg/Nm<sup>3</sup>. An increase in deactivation is to be expected with higher concentrations.

There are only a few cases known for example where the use of the catalytic process in lacquer drying (wire layquering etc.) and use of flame inhibiting solvents (e. g. hydrocarbon chlorides) has led to activity loss of the catalyst.

In principle either the complete removal of inhibitors or their substitutes or a reduction thereof to acceptable levels may be considered as a suitable measure for the elimination of temporary catalyst poisoning.