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Chemistry of Catalysts In Relation to Fire Protection

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FEATURES

ABOUT THE AUTHORS





CATALYSTS AND THEIR RESULTING ACTION called catalysis, play an important part in our daily lives. While we are not aware of this influence, it nevertheless extends to innumerable phases of our existence. Without catalysts many of our everyday products would be impossible, or at least, less common. Consider fertilizers, explosives and industrial chemicals which depend upon nitrogen as their main ingredient. The manufacture of these substances is made possible by the use of catalysts to "fix" atmospheric nitrogen and to prepare synthetic ammonia, as well as nitric acid. Another case in point is the catalytic cracking of petroleum to produce high grade gasoline. Production of synthetic rubber, sulfuric acid, plastics, dyestuffs, synthetic shortening (Crisco, etc.) further illustrate this application. Even our digestive processes depend upon operation of a group of catalysts called "enzymes," without which foods such as starch, proteins and oils could not be absorbed by our bodies.

There is no doubt of the importance of catalysts to the average person. To the fire protection engineers, to those in the fire service, they become so much more important, because the very existence of their occupation concerns itself with the outbreak of fire and explosion, both of which could well be impossible without catalysis. On the other hand, catalysis plays an important part in the control of this very adversary, as we shall see later in this discussion.

It is the purpose of this article, then, to consider some basic information concerning catalysts and their action as they affect our profession, so that this knowledge may be applied to solving some of the problems in the struggle to protect life and property from the ravages of fire.

Theory of catalysts

A catalyst may be defined as a substance which has a pronounced ability to alter the speed of chemical reactions without suffering any permanent change, itself, in the process.

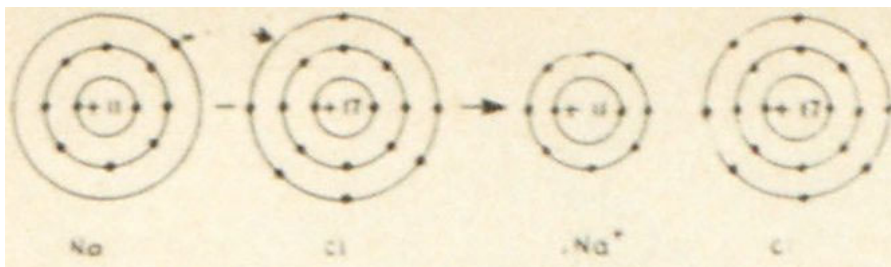
A knowledge of chemical changes and how they take place is a necessary prerequisite to understanding the part played by catalysts in affecting their rates of speed.

We are all familiar with the fact that matter is constantly undergoing changes and that these changes can be classified as either physical changes or chemical changes.

A physical change is one in which certain properties of matter, such as color, state or density are temporarily changed by a change in conditions. When the original conditions are restored, the original properties return. Catalysts do not affect this type of change.

A chemical change, on the other hand, is one in which the composition of matter is altered and new substances with new properties are formed. A return to original conditions will not restore the original properties. Combustion, fire, explosion and respiration are examples of chemical changes. We know, too, that matter is made up of small particles called molecules, which exhibit the ordinary properties we recognize in different materials. The molecule, in turn, is made up of smaller particles called atoms, the smallest particles of matter that can take part in the process we call chemical change. Atoms are made up of particles, electrical in nature, and consist of a positive nucleus surrounded by a group of negative particles, called electrons,

which revolve about the nucleus in orbits, much like the planets around the sun. Furthermore, the atom is so constituted that the positive charges just balance the negative charges and result in an electrically neutral atom. By disturbing this relationship, as, for example, when molecules collide with sufficient energy to dislodge electrons, chemical change is brought about. One atom loses electrons, becoming positively charged; the other gains electrons, becoming negatively charged. The attractive forces between the negative and positive atoms (ions, as they are called) hold the two together to form a new substance.



The speed with which such changes are brought about varies widely. For example, solid, massive wood burns at a low rate of speed. This same wood, when finely divided and suspended in air, can react with the speed of an explosion. Furthermore, wood can exist in contact with the air for years without apparent change. Application of heat is necessary before self-sustained burning can be attained.

This leads to the conclusion that certain agencies can be brought to bear upon the reactants so that their rate of change can be greatly affected. Of the many factors that can alter the rate of chemical change, the four of primary interest to the fire service are: concentration of reactants, temperature, contact of surface, and catalysis.

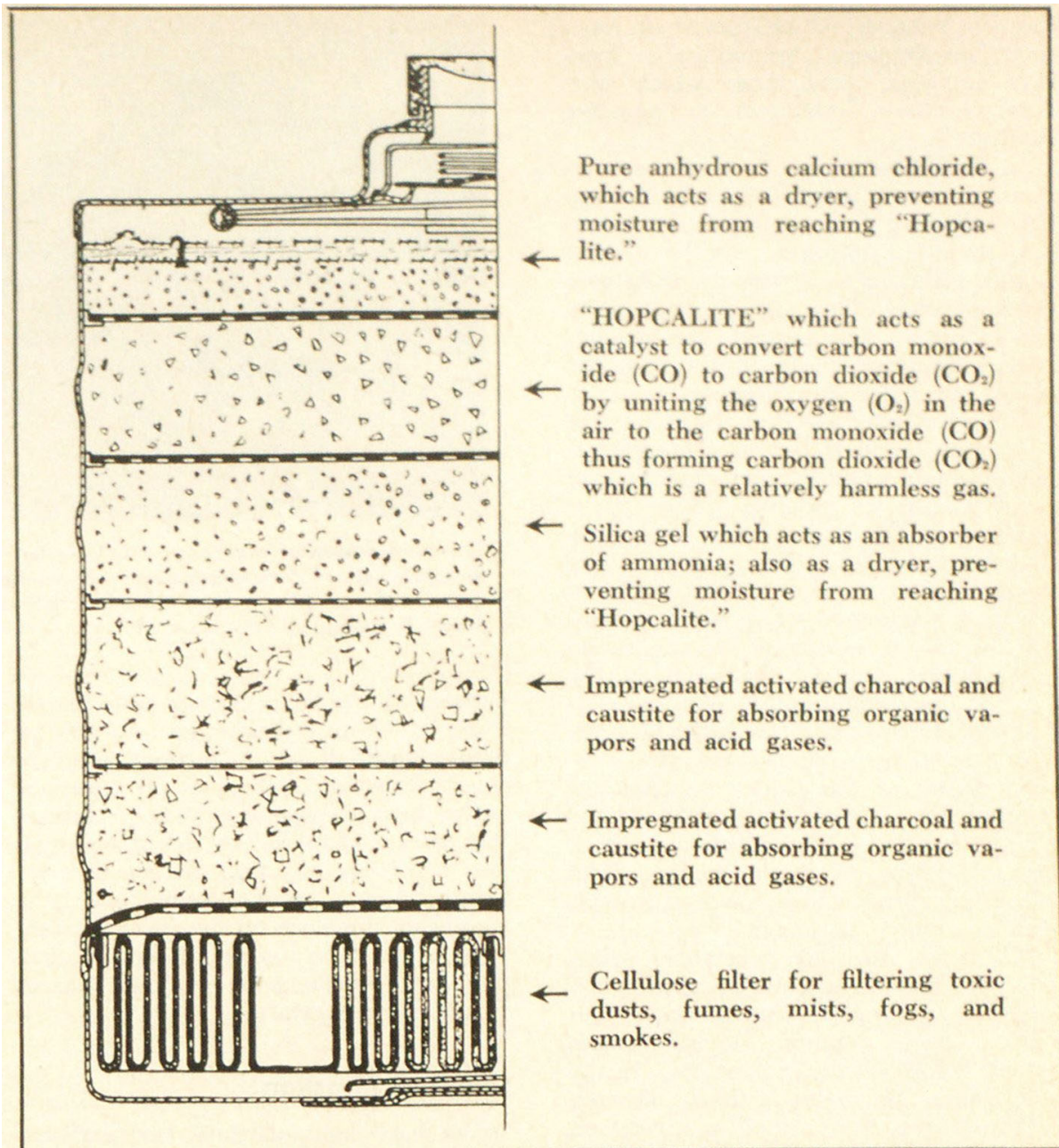
For our present purpose, only the last —catalysis—will be discussed.

In the preparation of oxygen from potassium chlorate, the gas is evolved with great difficulty even when the substance is heated almost to its melting point. In the presence of a small amount of manganese dioxide, however, oxygen is set free in large quantity at a much lower temperature. This classical experiment is familiar to all who have taken high school chemistry. Berzelius, who first gave the name to this phenomenon, likened the action of a catalyst to that of a lubricating oil on machinery. We, in the fire service, may compare this effect with that which a chief officer has, in speeding up the action of a group of slow moving fire fighters, simply by his appearance on the scene. A remarkable transformation takes place; the work is done faster and better merely by virtue of the presence of the chief who took no actual part in the process. Thus it is with catalysts.

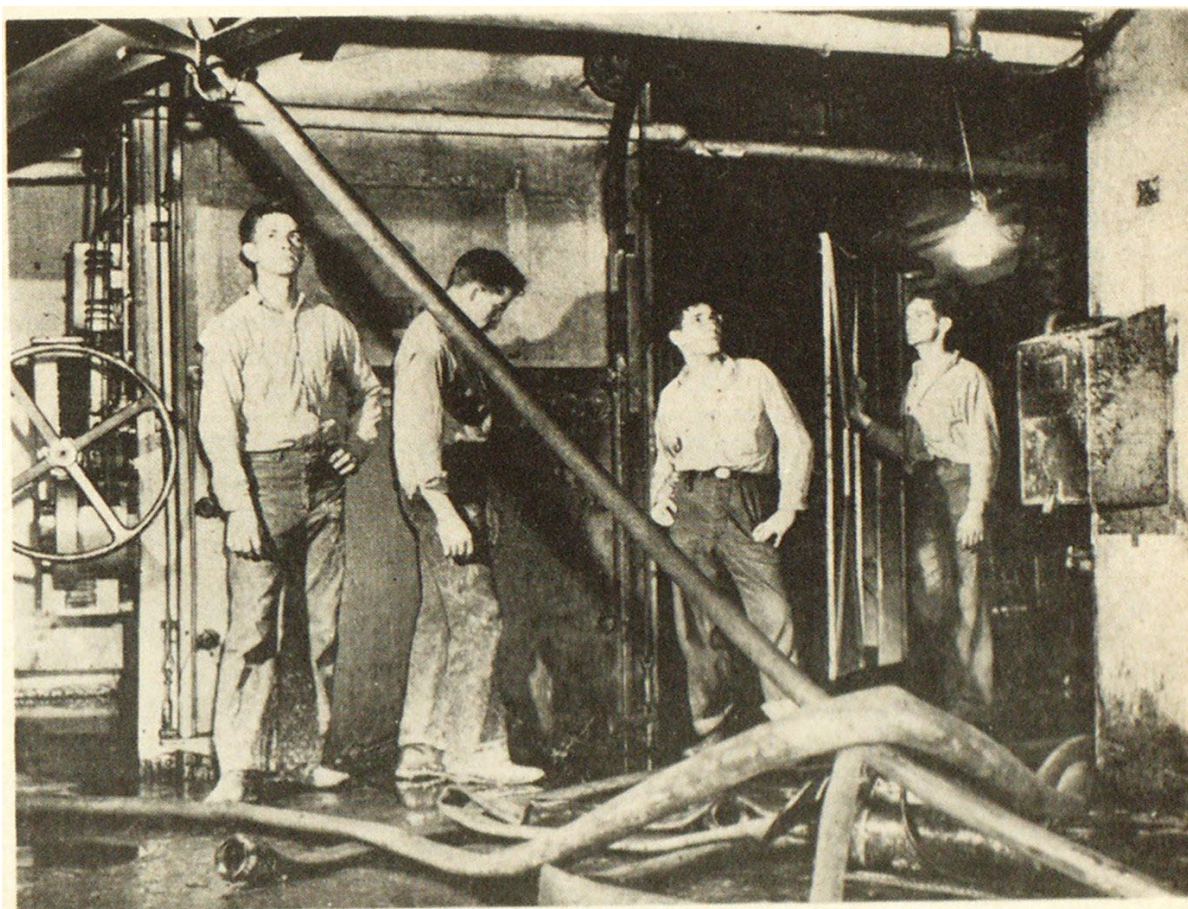
It requires only a small amount of a catalyst to greatly alter the speed with which large amounts of reactants undergo chemical change. The decomposition of acetaldehyde, for example, increases in speed by 10,000 times the normal rate in the presence of a small amount of iodine vapor. Hydrogen peroxide in water solution will decompose in the presence of minute quantities of copper compounds, dissolved when the water is distilled in copper coils or vessels.

Catalysts also exhibit a high degree of selectivity in their influence. A catalyst which is effective on one chemical change may not affect any others. In addition to this, certain catalysts exhibit their effects only at certain temperatures and are inactive at others.

They can either accelerate chemical changes or slow them down. We call those substances which speed up reactions, "accelerators," "promoters" or "positive catalysts," and those which slow down reactions, "inhibitors" or "negative catalysts."



—Courtesy Mine Safety Appliances Company



In some cases, a product of the reaction may act as a catalyst, in which case it is called an "autocatalyst." For example, oxides of nitrogen may be present in nitrocellulose as a product of its own decomposition. These oxides catalyze the decomposition and promote the detonation of the nitrocellulose. In this case, the oxides are called autocatalysts.

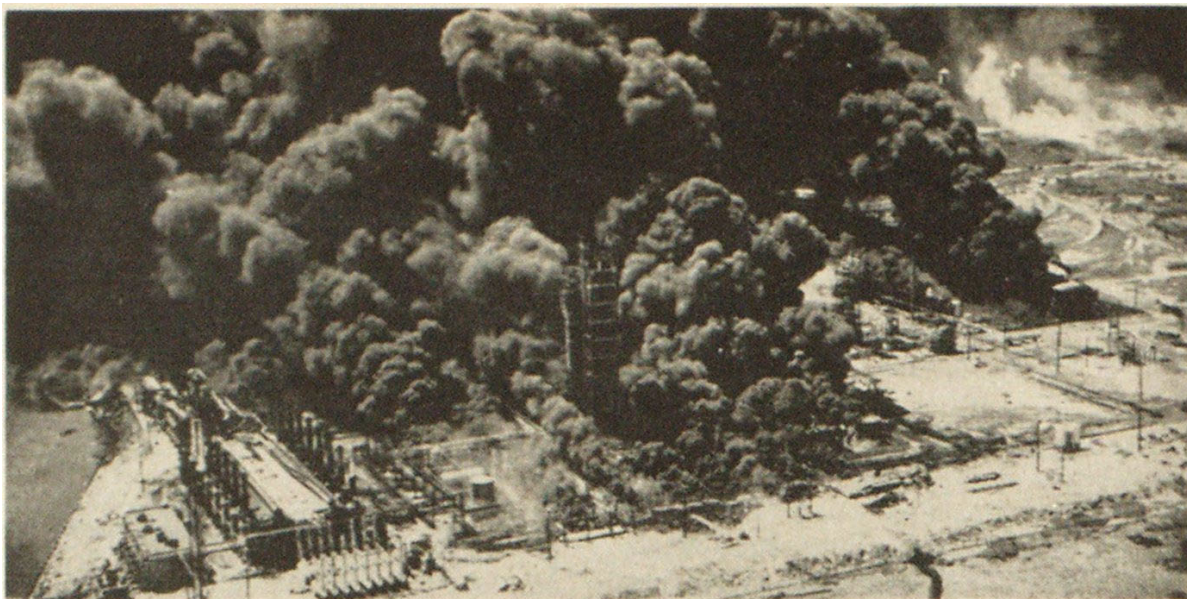
Inhibitors may act directly in slowing a reaction, as in the case of lead tetraethyl which prevents the oxidation of hydrocarbons in gasoline during compression of the gases before the spark is introduced. In other instances, the negative catalysts may act indirectly by affecting the action of a positive catalyst, which is normally present as an autocatalyst. This is illustrated in the case of the decomposition of nitrocellulose with formation of the oxides of nitrogen. In the presence of urea, the catalytic power of the oxides is destroyed so that the material is stabilized and may be handled safely. Substances which act to destroy or minimize the effect of a catalyst are called, "catalyst poisoners," or simply, "poisoners."

There are also some substances which are not themselves catalysts, but when added to a catalyst, they increase their power. Such catalyst intensifiers are called "boosters" or "supporters." In the preparation of ammonia from nitrogen and hydrogen, iron is used as a catalyst. In addition to this, alumina is used to boost the ability of the iron to catalyze the reaction.

It is also a fact that various surfaces can catalyze certain reactions. In combustion reactions especially, the catalytic action of surfaces plays an important role. Investigations have shown that a large heated mass of iron will accelerate the burning of illuminating gas and air. It is also known that practically all surfaces will catalyze the burning of hydrogen and carbon monoxide in air. The surfaces in these instances act in this way even though they are at temperatures below the ignition point of the gases. As the temperature of the surface increases, the power to catalyze reactions also increases, so that when incandescence is reached, the effect upon combustion reactions approaches astronomical proportions. Some of the unexplained and mysterious explosions that have occurred at fires after they were burning for a period could probably be traced to this property of heated surface.

The ability to adsorb gases is exhibited by such surfaces on which these gases are concentrated and activated. (Adsorption is "the adhesion in an extremely thin layer, of the molecules of gases, of dissolved substances, or of liquids to the surfaces of solid bodies with which they are in contact.") The attractive forces existing on the surface break down the molecular structure and release the elements in the atomic or "nascent" state, in which condition they are highly reactive. Some surfaces are

capable of adsorbing certain gases in volumes which exceed their own volume by many hundredfold. A further result of this concentration of gases on a surface is that heat is released from the condensing gases and added to the other agencies which are affecting the speed of reaction. Heat, as we know, exerts a significant influence on the speed of reactions, for some cases of combustion, doubling the speed for every 18 degrees F. rise in temperature.



Catalysts in action

We have learned, then, that catalysts can increase or decrease the speed of reactions. In the first service we are particularly concerned with the chemical reaction called combustion or burning. It has been known for a long time that most cases of combustion cannot proceed unless a minute amount of water vapor is present to catalyze the reaction. For example, if a mixture of carbon monoxide and oxygen be perfectly dried by laboratory methods, it is almost impossible to have them react. When a small amount of water vapor is introduced, then the mixture can easily be ignited and, exploded.

At first thought, there seems to be no practical significance in this fact because it is difficult to keep any such mixture free from moisture. However, it is not beyond the realm of possibility that some day a substance will be found to destroy or curtail the power of water to catalyze these reactions. When that bright day arrives, the fire service will have at its disposal the best fire fighting tool since man first discovered that water could extinguish fire.

There is still another practical implication in this fact which may be useful to us at this time. It is well known that, as the temperature of the air drops, the amount of water vapor in it also drops, so that at the temperatures prevailing in arctic regions, so little water vapor is present that sparks of low intensity will not ignite some ordinary gas-air mixtures. With the increased activity going on in these regions, it is both a happy and an unhappy fact that this is so. It is happy for the fire protection engineer in that ordinary sparks may not ignite combustible gas-air mixtures, thereby decreasing the chances of fire. It is unhappy for the transportation engineer in that an intensified spark is required to ignite the gasoline-air mixture in internal combustion engines.

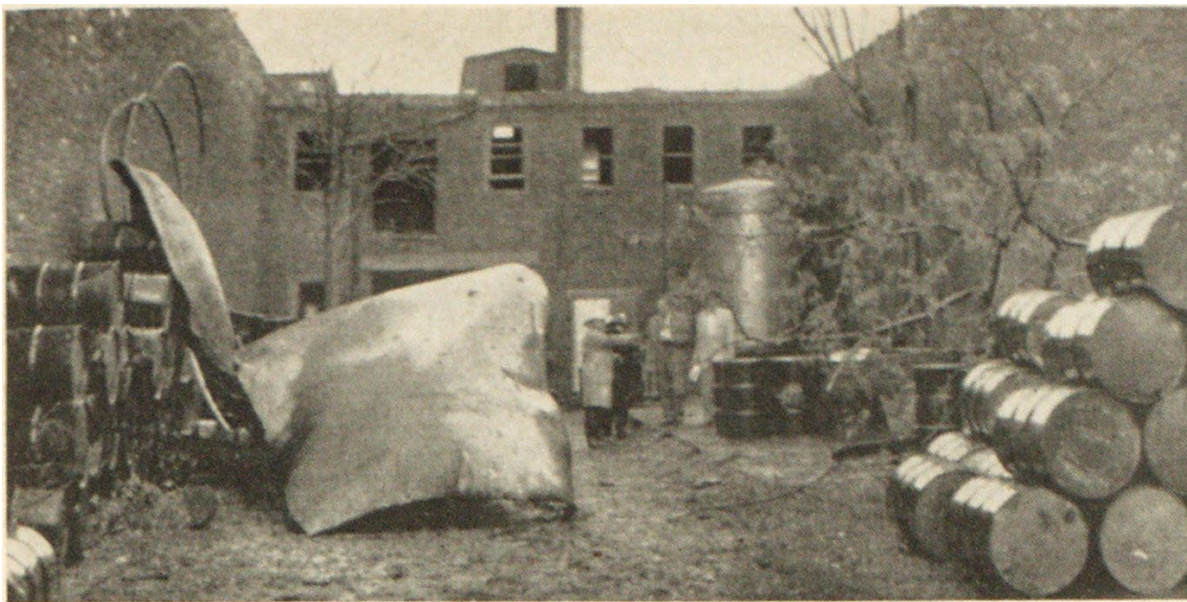
Surfaces, as we have seen, also exert powerful influences on combustion reactions. In this respect heated metals, especially iron, can catalyze many reactions which might proceed normally at much lower speeds. For example, hydrogen and oxygen can remain unchanged while mixed at ordinary temperatures. Only when the temperature is raised to about 1000 degrees F. do they interact and explode violently. Certain surfaces, however, will cause this ignition even at ordinary temperatures. At elevated temperatures the reaction takes place with added violence.

A practical application is made of this fact in one brand of cigarette lighter, in which a hydrocarbon mixture is drawn through a special metal mass, which catalyzes oxidation of the vapors to produce a flame.

During the progress of an actual fire, it is difficult or almost impossible to know exactly the conditions under which chemical reactions are proceeding. Oxidation reactions, we know, are subject to catalytic influences. There are numerous other reactions, decompositions and interchanges which can proceed simultaneously and which are also subject to catalytic

influences. At the same time, we do not know what catalysts may be present to exert their powers. Yet in numerous fires some very commonly known catalysts are in evidence. Heated iron and other metals are almost always present. Copper oxide, an excellent catalyst in some reactions, may be formed by oxidation of copper during a fire, adding its influence to the reactions. Aluminum and its products, which catalyze organic reactions, are also commonly found, and may adversely affect organic products of combustion, to add fury to an already violent reaction.

Products of ordinary wood fires, as a further illustration, contain substances which belong to a class of organic catalysts called aldehydes, as well as acetic acid by-products, and possibly ketones, which are also classed as organic catalysts.



—Philadelphia F. D. Photo

We have already considered the action of the oxides of nitrogen in promoting the detonation of nitrocellulose. Under ordinary conditions, urea inhibits their action, but under fire conditions, it is entirely probable that these oxides are formed so fast and in such quantities as to overcome the influence of the urea. The violence exhibited by a burning mass of celluloid could very well be traceable to this.

Later, some other cases of catalytic action will be taken up, but at this time consideration must also be given to those actions which tend to inhibit or slow down combustion reactions.

The most familiar example of an inhibiting agent is lead tetraethyl in ethyl gasoline, which was mentioned before. Without the use of this product, the internal combustion engine would be a less efficient machine because the motor would be subjected to pre-ignition knocks and loss of power. Another familiar inhibitor is acetanilide which keeps ordinary hydrogen peroxide from decomposing too rapidly. Others are compounds used to keep rubber tires from aging prematurely and sodium benzoate to keep foods, such as ketchup, from spoiling.

Less familiar to us is the fact, as suggested by some authorities, that at high temperatures, nitrogen in the air acts as an inhibitor for certain combustion reactions. This function is in addition to that of diluting the oxygen. It is entirely possible that nature, in its orderly design, intended nitrogen to be such an inhibitor to prevent a general conflagration which could envelope the entire earth, once having had a start. The elements of such an inferno are ever present, the oxygen of the atmosphere in intimate contact with combustibles (forests, gases, etc.), and the heat for ignition supplied by the first lightning flash. We find, however, that although fires can be started easily and will continue to grow, they never reach the point of involving the entire globe. It may be that the inhibiting powers of nitrogen (and perhaps other atmospheric substances) do not exert themselves until a certain temperature or quantity of heat is attained, when the reactions are inhibited and held in check. This could also explain why nuclear explosions, with temperatures ranging to tens of thousands degrees, do not involve the entire atmosphere.

In actual fire extinguishment use is made of catalytic action. The so-called loaded stream extinguishers are effective on fires because of the inhibiting power of certain alkali salts dissolved in water. On Class "A" fires, these extinguishers put out the

flames rather suddenly and in addition, exert a definite fireproofing effect, by preventing flash backs. On Class "B" fires there are no smothering vapors produced, but the flames are quickly extinguished. In both cases, the effective extinguishing action is attributed to the catalysts in the stream which inhibit oxidation.

This fact was discovered quite by accident about 25 years ago, by two researchers, Thomas and Hochwalt, when they noticed that gasoline flames were suddenly extinguished by a water solution of sodium potassium carbonate. They then conducted rather exhaustive tests to find other substances which exhibited this property. The results obtained were so startling, as to be unbelievable. For example, a 20 per cent solution of potassium nitrate in water, extinguished an oil fire with greater ease than a like volume of carbon tetrachloride!

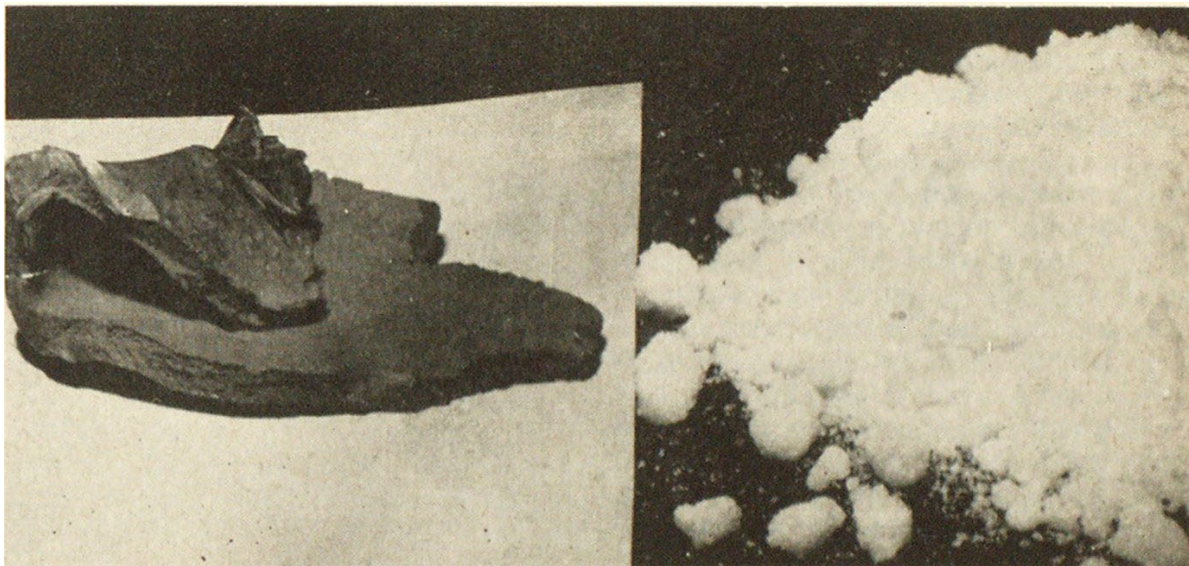
They found, also that with few exceptions, only compounds of the alkali metals possess this effect. It also appeared that the extinguishing effectiveness increases with increase in atomic weight of the alkali metal, and that the oxygen-bearing radicals were generally more effective.

The loaded stream extinguishers are a practical application of these investigations.

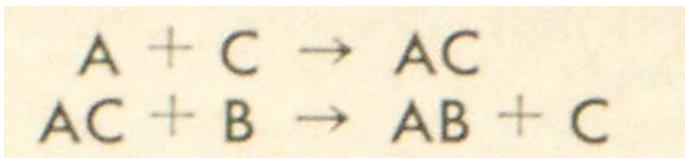
Some authorities have also shown that carbon tetrachloride could extinguish burning charcoal when present in air in quantities of about 5 per cent. In this case the oxygen percentage is reduced by only 1 (21 per cent to 20 per cent) and the extinguishing action cannot be attributed to dilution or smothering. It is certain that this is due to a negative catalytic action exerted by carbon tetrachloride vapors.

The British Department of Scientific and Industrial Research, Fire Research Technical Paper No. 2, states concerning the action of halogenated hydrocarbon extinguishing agents, such as carbon tetrachloride, "Their extinguishing capacity depends more particularly on their influence on the chemical reactions involved in the propagation of the flame." They also state that some other halogenated liquids have extinguishing powers superior to carbon tetrachloride, particularly chlorobromomethane and trifluorobromomethane.

In the field of fire fighting an important application is the catalytic effect in a filter-type gas mask for operating in atmospheres containing dangerous amounts of carbon monoxide. In this case, the gases breathed are drawn through a series of filtering media, of which the most important is a material called "Hopcalite." This substance is a mixture of metallic oxides of manganese, copper, cobalt and silver, which acts to catalyze the union of carbon monoxide with the oxygen in the air to form carbon dioxide, which can be breathed into the lungs without injury. Water in this case prevents the Hopcalite from catalyzing the reaction, and is therefore removed from the gas mixture by first passing through a layer of calcium chloride.



—Photo by U. S. Coast Guard



Catalytic decomposition

The examples cited seem to be ordinary in nature and do not stimulate any great interest on the part of the average fire fighter. Only when some extraordinary disaster strikes, do we stir from our lethargy and make any real attempt at applying known scientific principles to finding the causes. Such a case, with which we are all familiar, is the chemical explosion which occurred two years ago in Philadelphia, and took the lives of ten fire fighters. A mixture of chlorinated solvents (orthodichlorobenzene, ethylenedichloride and propylenedichloride) was stored in a poorly purged aluminum tank, that had previously held coconut oils. It is held that a small amount of moisture present in the tank may have acted upon the chlorinated hydrocarbons and produced hydrochloric acid, in a process called hydrolysis. This acid then reacted with the aluminum to form aluminum trichloride, which acts as an autocatalyst and caused an accelerated decomposition of the mixture with release of excessive heat and pressure, which were prevented from escaping because of a clogged vent. As a result the tank ruptured and trapped the fire fighting force before they knew what was happening. Another possible explanation is that heat from the sun beating down on the tank caused a reaction between propylenedichloride and aluminum with the formation of aluminum trichloride catalyst.

Any compound of aluminum, magnesium or other light metals, and halogen derivatives, or any potential combination of these chemicals, should be viewed with suspicion and kept under careful control.

Another example of accelerated decomposition occurred on the aircraft carrier U.S.S. Leyte several years ago (and also on the U.S.S. Bennington), when a hydraulic ram system using hydrocarbon oil and compressed air exploded and caused a severe fire and loss of life. Investigators believe that under the conditions of temperature, pressure and frequency of use that existed, decomposition in the oil may have resulted in the formation of organic peroxides and aldehydes, which could have catalyzed the reaction to the point of detonation. As a result, the Navy is now using a noncombustible water solution of glycol in the rams, which is believed to be free from the danger of accelerated decomposition initiated by catalysts.

It should be pointed out that conditions of heat and pressure affecting organic materials must be considered dangerous because they can cause the formation of some product which has the potentialities of a catalyst.

While on the subject of heat and pressure, it is well to mention the Texas City disaster of 1947. It is known that ammonium nitrate was undergoing decomposition at the time of the explosion. In fact, fire fighting was in progress for over an hour and the detonation took place suddenly and without warning, shortly after the holds were battened down. While ammonium nitrate was considered a rather safe material until that time, it has been shown in laboratory tests that a violent explosion can be brought about by subjecting the material to certain conditions of heat and pressure, together with confinement of the products of decomposition. In this case, it is likely that some products of the decomposition, possibly oxides of nitrogen, act to catalyze the reaction to the point of detonation.

This theory is further borne out by results of tests by the U. S. Department of Commerce following the Texas City explosions. All attempts to explode ammonium nitrate by heating in test bombs were unsuccessful when in contact with air. However, when the atmosphere in the bomb was replaced by a mixture of carbon monoxide and nitrous oxide (products of its decomposition) then the material exploded violently. One very important recommendation made is that confinement of the products of decomposition and combustion must be avoided, in case of fire involving ammonium nitrate. Authorities further state that no instance is known of an explosion being caused by heat or fire alone.

The number of catalytic reactions that can possibly occur under fire conditions is so large that space permits mentioning but a few. An exceedingly common occurrence is that of activated charcoal in condensing combustible gases and oxygen on its surface and causing fire to break out in a process called "pyrophoric action." Activated charcoal can easily be formed by low heat acting on carbonaceous material, such as wood. A steam pipe or chimney flue in contact with wood trim can produce this form of charcoal.



Charcoal, embers and coke, which are produced by the destructive distillation of carbonaceous material during a fire may act as catalysts in speeding the combination of hydrocarbon gases, which are themselves released in the process, with the oxygen of the air.

In the field of fire prevention, too, a knowledge of catalysts is useful. For example, knowing what normal catalysts are stored in a plant will give some idea of how storage facilities should be arranged so that the catalyst and the material it acts on can be isolated. In addition, many catalysts themselves are highly hazardous chemicals. Plastics catalyzers such as benzoyl peroxide and similar materials, for example, are thermally unstable at temperatures as low as 165 degrees F.

Future of catalysis in the fire service

It is obvious from our discussion, that catalysts have an important bearing on the fire service. Because they are subject to definite natural laws, it follows that we can hope to put them to use, under certain conditions, to aid us in our fight against fire. Industry, already far ahead of us in the use and knowledge of catalysts, has progressed to the point where predictions can be made as to the proper catalyst needed to activate a specific reaction. Perhaps, in the not too distant future, we too, may couple scientific research with inventive genius to make catalysts do a better job for us. Like the far-sighted industrialists, the authors have made some predictions which they believe will come true, provided enough encouragement is given to those who wish to apply scientific principles and methods to solving the problems of the fire service. Some of these are listed below for further contemplation and study.

1. Use can be made of catalysts as an extinguisher, perhaps in the form of paint, which would release an inhibitor at a certain temperature to stop any fire which breaks out. A similar use is the incorporation of an inhibitor dissolved in water in a conventional sprinkler system to exert its effect through operation of sprinkler heads.
2. A detection device which would transmit an alarm when exposed to certain gases, heat, smoke or fumes. Selective catalysts might be used to guard against specific hazards. Perhaps they would shut down air conditioning plants, close fire doors and disconnect power. It must be pointed out that they would be less likely to be accidentally activated than light sensitive devices (photoelectric cells).
3. An automatic design for feeding a small amount of inhibitor into fire streams, so that a minimum size fog stream would rapidly extinguish a fire and prevent flash back without subjecting the fire fighters to any danger.

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CHEMISTRY OF CATALYSTS

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1. A grenade-type device which could be thrown or fired into a burning building to bring the fire under almost immediate control. This bomb idea could be extended to use over forest and brush fires.
2. Use of selective catalysts to render harmless the gases produced by combustion, so that rescue, fire fighting, or salvage operations can be conducted in safety. A further application of this is where industrial gases or chemicals make fire fighting or industrial operations dangerous.
3. Use of small amounts of catalysts in ordinary air to prevent oxygen from combining with dangerous materials, which now require use of inert gas protection such as carbon dioxide.
4. A further extension of this idea so that the interior atmosphere in factories and plants conducting extremely hazardous processes (oil refineries, explosive, flammable chemicals) would be made inert as far as combustion is concerned, but will allow normal respiration by workers. Highly selective catalysts could be used.
5. The mandatory incorporation in each building of an automatic inhibitor which could be set in operation by high frequency radio waves transmitted from a central fire department communication center.

Conclusion

Some of the ideas set forth here are definitely within the scope of practical application. As a matter of fact, several devices making use of these facts are now on the market. For example, the Frigidaire Division of General Motors has just produced a new smokeless oven, which employs a special wire filter, heated to 650 degrees F. At this temperature it catalyzes the conversion of smoke into harmless amounts of carbon dioxide and water vapor. Another application is one type of combustible gas indicator, in which the oxidation of combustible hydrocarbon gases are catalyzed by a special wire unit, changing its resistance, and registering its concentration on a dial. Several years ago a sprinkler system using a special solution of catalytic chemicals was produced.

It must be pointed out again, that such applications of known scientific principles are entirely feasible and it is believed that someday enough knowledge concerning this mysterious and fascinating world of catalysts will be accumulated to solve each of the problems involved. Our hope for this lies in the open mind, the eager spirit, the insatiable curiosity, the painstaking scientific approach, of the young men in the fire service and the research laboratories of the future. In that day and age the fire service may move out of the fire stations and into the laboratory to take its rightful place beside the scientists. Its members

may then serve the citizens primarily in the capacity of inspectors and investigators whose duty it will be to see that no outbreak of fire occurs.

Employed in this way, the future fire service engineer could well be described in the words of Dryden:

"Happy the man who, studying nature's laws,

Through known effects can trace the secret cause."

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